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Treatment of industry wastewater by adsorption using some Iraqi clays

A Thesis Submitted to the Council of the College of Science,
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the Degree of Master of Science in Chemistry

by

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بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

﴿وَٱصۡبِرۡ لِحُكۡمِ رَبِّكَ فَإِنَّكَ بِأَعۡيُنِنَاۖ وَسَبِّحۡ بِحَمۡدِ رَبِّكَ حِينَ تَقُومُ ٤٨﴾

صَدَقَ ٱللَّهُ ٱلۡعَظِيمَ

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Salam

Dedication

To the pure and pure souls, my mother and father, I ask Allah to have mercy on them and make their graves a meadow from the gardens of Paradise and gather me with them in Paradise.

To my loved ones, my children (Youssef, Sadeen, Rayahin, Maryam and Riam) and my wife.

To my strength in life, my brother(Basim).

To the kind hearts, to the lovely people with whom I spent the most precious moments in my life. My teachers and my friends.

I dedicate my work

Salam

Supervisor Certification

We certify that this thesis (**Treatment of industry wastewater by adsorption using some Iraqi clays**) was carried out under our supervision in Chemistry Department, College of Science, Diyala University in partial fulfillment of the requirement for the degree of master of science in chemistry by the student (**Salam Mohammed Malih**).

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Abstract

This thesis investigated the use of Attapulgite and Flint Iraqi clays as cheap and environmentally friendly adsorbent surfaces for removal of copper, chromium, and zinc metals from industrial wastewater. The influence of clay amount, temperature, equilibrium time, and solution pH on adsorb of Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clays from their synthetic solutions in mono-system were studied by batch method. Then, the optimum conditions were determined and applied for industrial wastewater samples. The results showed that the removal efficiency of Attapulgite clay higher than Flint clay, and the maximum capacity of adsorption of Cr (III), Cu (II), and Zn (II) ions on the Attapulgite clay is in the following order: (Cr (III) > Cu (II) > Zn (II)).Whereas, on the Flint clay is in the following order: (Zn (II) > Cu (II) > Cr (III)). pH had a major effect upon adsorption of Cr(III), Cu(II), and Zn (II) ions in both systems. Adsorption of Cr (III) and Cu (II) ions increased as pH increased, with the best adsorption of Zn (II) ion occurred at pH = 4.

Kinetics were described using pseudo first order, pseudo second order, and intra-particle diffusion models. Experimental results fitted pseudo second order well and agreed with the intra-particle and simple external model.

The experimental results for adsorption of Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clay were achieved and applied to Langmauir, Freundlich, and D-R isotherms at two temperatures (298 and 318)K. The adsorption process results were agreed with the Freundlich isotherm model, but the Cr (III) ion on Attapulgite, which is fitted to the Langmuir isotherm model.

Thermodynamic functions, for instance, ($\Delta G°$, $\Delta H°$, and $\Delta S°$) were calculated from Van't Hoff equations for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint clays. The values of ($\Delta G°$) of Cr (III), Cu (II), and Zn (II) ions adsorption on Attapulgite and of Cr (III) and Zn (II) ions adsorption on Flint were negative, suggesting a spontaneous adsorption process. In contrast, the values of ($\Delta G°$) of Cu (II) ions adsorption on Flint clay were positive, suggesting a non-spontaneous adsorption process. On the other hand, ($\Delta G°$) values were between (-45.378 to 4.1313) $kJmol^{-1}$ at all measured temperatures, indicating that the adsorption process was physisorption. The enthalpy values ($\Delta H°$) of Cr (III), Cu (II), and Zn (II) ions adsorption on Attapulgite and of Cr (III) and Zn (II) ions adsorption on Flint were positive, suggesting an endothermic adsorption process. In contrast, the enthalpy values ($\Delta H°$) of Cu (II) ions adsorption on Flint clay were negative, suggesting an exothermic adsorption process. The entropy values ($\Delta S°$) of Cr (III), Cu (II), and Zn (II) ions adsorption on Attapulgite and of Cr (III) and Zn (II) ions adsorption on Flint were positive, suggesting an increase in randomness. While, the entropy values ($\Delta S°$) of Cu (II) ions adsorption on Flint clay were negative, suggesting a decrease in randomness.

Using the batch method, optimal conditions were applied onto an Al-Quds power station wastewater sample. The results showed that the removal percentage on Attapulgite was perfect and followed the order (Cr > Cu > Zn). while the removal percentage on Flint was lower and followed the order (Zn > Cu > Cr). As a result, the Attapulgite clay shows removal efficiency higher than Flint clay, and can be used in treatment industrial wastewater polluted by metals under study in many industrial fields, especially electrochemical coating plants.

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List of Symbols and Abbreviations

Abbreviation	*Definition*
AAS	**Atomic absorption spectrophotometer**
AFM	**Atomic force microscope**
A-HDTMA	**Attapulgite-hexadecyltrimethylammonium bromide**
D-R	**Dubinin-Radushkevitch isotherm**
C_e	**Equilibrium concentration of adsorbate**
C_t	**Concentration of adsorbate after any time**
C_0	**Initial concentration of adsorbate**
Fig.	**Figure**
E	**main energy of sorption**
ICP-MS	**Inductively coupled plasma-mass spectrometry**
K	**Thermodynamic equilibrium constant**
k_1	**Pseudo-first order rate constant**
k_2	**Pseudo-second order rate constant**
k_{id}	**Diffusion constant**
K_f	**Freundlich constant related to adsorption capacity**
K_L	**Langmuir equilibrium constant related to energy of adsorption (L/mg)**
L.O.I	**Loss on ignition**
m	**Weight of adsorbent**
min.	**Minute**
n	**Freundlich constant related with adsorption intensity**
q_{max}	**Adsorption capacity of the adsorbent at equilibrium time**
q_e	**Amount of adsorbate per weight of adsorbent at equilibrium**
R	**Gas constant**
R^2	**Correlation coefficient**
%R	**Percentage removal of adsorbate**
RMS	**Root mean square**
Rpm	**Revolution per minute**
R_L	**Equilibrium factor**
T	**Temperature**
$t^{1/2}$	**square root of the time**

V	**Volume of solution**
Wt %	**Weight percentage**
β	**Constant related to sorption energy**
ε	**Polanyi potential**
ΔG^o	**Gibbs free energy change**
ΔH^o	**Enthalpy change**
ΔS^o	**Entropy change**
λ_{max}	**Maximum wave length**

Chapter One

(Introduction)

1.1 Pollution

Pollution is defined as the accretion and harmful effects of pollutants as well as other components on public health, as well as the environment. Pollution of environment is a very rigid and challenging subject [1]. Controlling environmental contamination has come to be a major issue in developing states, with water pollution and air pollution being the two greatest serious issues. Burning causes air pollution, especially in forests, whereas wastewater pollution is caused by industrial discharge, commercial buildings, and government institutions that use water for a variety of purposes[2].

The present of heavy metals like as chromium, copper, zinc cadmium, lead, and others is a major source of worry in scientific studies due to the extreme living health risks associated with heavy metals, as well as their toxic effects[3,4]. Heavy metal pollution of aqueous environments is a global environmental concern due to its harmful effects and accretion during the food chain [5,6]. Heavy metals are essential contaminants in groundwater, marine, industrial, and sometimes even treated wastewaters [7]. Phenols are also among the most common organic contaminants in industrial effluents [8]. Heavy metals and phenols are discharged into the environment by industries such as power stations, fertilizers, painting, petroleum refining, steel, coal tar, tanning, pharmaceuticals, pesticides, and others [9]. This necessitates the development of techniques for identifying, quantifying, and removing heavy metals and phenols from industrial effluent [10].

Adsorption is being considered as a significant technology for removing pollutants from wastewater. Adsorption is still the best method for wastewater treatment when compared to other chemical, physical, and biological techniques available due to high efficiency, flexible design, simplicity and easy operation. The adsorption could produce no or tiny harmful chemicals and this reduced initial and maintenance costs [10].

Clay as adsorbents have benefits over other available commercially adsorbents due to their cheap, wide availability, large surface area, good adsorption characteristics, non-toxic nature, and big ion exchange ability. [11]. Clay minerals and clay have a difficult porous structure and a tiny particle size, and a large surface area, allowing for robust chemical and physical interactions with dissolved types. These interactions are caused by crystallinity, adsorption or cation exchange, and electrostatic repulsion. The extremely porous surface with a force of attraction implies that the bonding will be strong as well[12].

The current study focuses on using Attapulgite and Flint clays as adsorbent surfaces to removal chromium, zinc, and copper metals from industry wastewater. In contrast, the effect of pH, temperature, contact time, and clay dosage upon removal of metal in a mono-system was investigated. Thus, apply optimum conditions on industry wastewater sample which was taken from water contaminated with crude oil used in the fuel washing unit at Al-Quds power station, located northeast of Baghdad.

1.2 Literature survey

(Potgieter et al., 2006), Used palygorskite clay as an adsorbent surface to removal nickel, lead, copper, and chromium ions from aqueous medium. The adsorption data agreed with Freundlich and Langmuir models. Metals adsorption occurred in the following order: (Pb > Cr > Ni > Cu) [13].

(Han et al., 2006), Studied Chaff's ability to adsorb Cu (II) and Pb (II) ions in fixed bed. Effect of significant factors like pH, flow rate, influence of solution concentration, and ion coexistence effect have been investigated. Adsorption/desorption recycles of chaff were also observed, indicating that chaff can be recycled to removal heavy metals [14].

(Al-Kaim et al., 2007), The researcher investigated the adsorption of phenol from aqueous medium by Attapulgite clay and Attapulgite-urea-formaldehyde polymer (AUFP) as adsorbent surfaces. The experimental results revealed that the adsorbents' ability to adsorb phenol is in the following order: AUFP < Attapulgite, the adsorption of phenol on the Attapulgite and AUFP was fitted with the Freundlich model. The adsorption process was endothermic and kinetic studies indicated that adsorption was fitted with pseudo first order [15].

(Hussain et al., 2007), Studied Cobalt (II) ion adsorption from aqueous medium using Attapulgite, Bentonite, and Kaolin as cheap adsorbent surfaces. The aim of the study is to look for cobalt (II) ion adsorption surfaces that are highly applicable to the treatment of aqueous solution contamination in nature by this heavy metal ion [16].

(Bedelean et al., 2009), The removal of Cd (II), Pb (II), and Cr (III) from wastewater using Bentonite clay from Cluj County was investigated. The effect of dynamic and static working regimes on efficiency was investigated using wastewater of synthetic mono-components containing Cd, Cr, and Pb ions [17].

(Al-Jlil and Alsewailem, 2009), Studied removal of lead ion from wastewater by using three kinds of clays Khaiber, Baha, and Tabuk as adsorbent surfaces. The highest adsorption capacity was for Tabuk clay. Freundlich model of adsorption fits with the experimental results of treated Baha clay and untreated Khaiber clay, whereas Langmuir one fits with all treated clays[18].

(NAJI, 2009), Studied methylene blue dye adsorption from aqueous medium by using Attapulgite clay as a cheap adsorbent surface. The experimental results revealed that the perfect concentration of dye was 10 mg/L and the ratio of adsorption was 86.28%, the shaking time was 35 minutes, the best pH value was (8), and the adsorption process was endothermic[19].

(Mouhannd, 2009), Investigated removal of mercury ion from aqueous media using Bentonite clay as adsorbent. The results indicate that the concentration was 10 mg/L, with an adsorption ratio of 88.7% and an adsorption capacity of 0.444 mg/g that increased with temperature and was endothermic[20].

(Athraa,2010), Studied adsorption and desorption of Bisoprelolhemifumarats by using Kaolin and Attapulgite as adsorbent surfaces. The effect of drug concentration, ionic strength, contact time, pH, temperature and drug desorption from the two surfaces were investigated. Experimental data exhibited that the adsorption process fitted with the Freunlich model and adsorption was exothermic [21].

(Jassim et al., 2010), Studied zinc ions removal from industrial wastewater by unmodified wool fibers. Study aim is use a highly sensitive, usable and inexpensive normal substantial that has been effectively used for industrial wastewater, where zinc ion concentration has been decreased from (14.6 to 0.07) mg/L and contamination dangerous effect has therefore been decreased [22].

(Salim,2011), Studied (o-nitrophenol, m-nitrophenol and p-nitrophenol) adsorption from their synthetic solutions using Attapulgite and its modified form (A-HDTMA) as an adsorbent surface. The results exhibited that maximal capacity of adsorption for (m-nitrophenol o-nitrophenol, and p-nitrophenol) of two clays are in the order:(p-nitrophenol > o-nitrophenol > m-nitrophenol).The modification of clay by HDTMA improved adsorption capacities of nitrophenols, achieving equilibrium after shorter contact time compared with the unmodified Attapulgite [23].

(Talaat et al., 2011), Studied removal of Cr (III), Ni (II), Cd (II), Cu (II), Zn (II) and Pb (II) from polluted effluents by using fresh and treated Kaolin in addition to (Ca-B and Na-B) as an adsorbent surfaces. The experimental data exhibited that raw Kaolin performed best than acid-washed or calcinated Kaolin. Using Freundlich isotherm, adsorption of Cd (II), Cu(II), and Ni (II) was well described, while that of Pb (II) and Zn (II) matched well to Langmuir isotherm [24].

(Al-Sharify and Athab, 2012), Studied adsorption of p-chloroaniline (PCA) from synthetic solution by Attapulgite clay as an adsorbent surface. Thermodynamic factors like as (ΔG^o, ΔS^o, and ΔH^o) were determined and results indicated that the PCA adsorption was an endothermic process and a spontaneous on Attapulgite clay. Adsorption fits well with the Freundlich model[25].

(Abdalla and Al-Sharify, 2012), Investigated influences of dye contact time, concentration, and solution pH onto adsorption of terasil yellow (W-6GS) dye solution, as were the effects of base, acid, and salt concentrations on the adsorption process [26].

(Emad, 2013), Studied adsorption of copper (II) from wastewater by using activated carbon produced from expended lubricant oils via chemical modification as an adsorbent surfaces and a locally Bentonite. The results showed that clay adsorbs Cu (II) ions better than activated carbon, with a larger adsorption capacity. The experimental data exhibited that adsorption process fits well with Langmuir model and it was endothermic[27].

(Baqir et al., 2013), Studied adsorption of (R6G) dye upon low-cost adsorbent surfaces such as Attapulgite and Flint clays. The results showed that removal ratio for (R6G) dye at equilibrium by Flint and Attapulgite clays was 85% and 88%, respectively. Adsorption process was well described by Freundlich isotherm [28].

(Dakhil, 2013), Investigated adsorption of Cr (VI) from their synthetic solutions by spent tea leaves (STL) as an adsorbent surface. The experimental results exhibited that adsorption was agreed on a second order polynomial model and it was fitted with the Langmuir model. In optimal conditions, the maximum monolayer capacity was specified at 47.98 mg/g[29].

(Olaofe et al., 2015), Used a batch method to study the adsorption of Pb (II), Cu (II), Cd (II), and Zn (II) upon local clay from altered sites in Ekiti state. Using linear regression analysis, experimental results were connected with isotherms and kinetic models. Langmuir was fitted with adsorption results [30].

(Jasem, 2015), Studied adsorption of Cu (II) and Cd (II) ions from synthetic solutions by Bentonite clay and banana peels as adsorbent surfaces. The experimental results showed that ratio removal reached 98% and 77% for Cd (II) upon Bentonite and banana peels respectively and 99.5% and 80% for Cu (II) upon Bentonite and banana peels respectively at perfect conditions: metal concentration 5 mg/L, adsorbent quantity 2 g per 100 mL, pH = 5 and particle size 75µm. Adsorption data for Cu (II) and Cd (II) was fitted to the Freundlich isotherm model[31].

(Ghorbel-Abid and Trabelsi-Ayadi, 2015), Investigated the removal of Cr (III) and Cd (II) ions by landfill clays in Tunis's northwestern region. By using the batch method, they studied adsorption data for Na-purified and natural clays in synthetic solutions of Cr (III) and Cd (III). The contact time for Cr (III) ions with natural and purified clays was 60 and 15 minutes respectively. Meanwhile, the contact time for Cd (II) ions on natural and purified clays was 3.5 and 2 hour respectively [32].

(Ahmed, 2016), Studied the removal of Cu (II), Zn (II), Cd (II), and Pb (II) ions from their synthetic solutions using (Iraqi Bentonite, Iraqi Kaolin and Italian Kaolin) as adsorbent surfaces. Results also exhibited that the percent adsorption for removal of the most ions at (pH = 9, Temp.=303 K, and 10 min contact time) was 100%. The adsorption percentage increased with an increase in temperature and contact time[33].

(Sadiq, 2016), Studied adsorption of cefixime using Iraqi Attapulgite as a low cost adsorbent surface. Using the technique of UV-Vis spectrophotometry at (λ_{max} = 273 nm) under different conditions (contact time, temperature, adsorbent dosage, pH and ion strength), quantitative estimation of drug adsorption was performed. The experimental results showed that adsorption fitted with the Langmuir isotherm and the system was exothermic[34].

(Waheeb, 2016), Studied adsorption of direct blue (DB71) anionic dye from synthetic solutions by Flint clay as adsorbent surface. Under the batch adsorption process, contact time, pH, adsorbent quantity and temperature were assessed. Adsorption equilibrium results fit with isotherms Langmuar and Freiundlich. Sorption of the dyes onto Flint clay was endothermic and spontaneous [35].

(Lahieb, 2016), studied adsorption of Cu (II) ions from waste by modified and original sunflower stalks as adsorbent surfaces. Batch mode and fixed bed mode were used for operations. The experimental results showed that sunflower stalks, both modified and unmodified, are an effective adsorbent for copper removal from waste water. When the particle size was (2.36-4.75) nm, the bed depth was 35 cm and the influent flow rate of 4 L / hr., the percent of removal of copper reached 100% [36].

(Garba et al., 2016), Used defatted papaya seeds (DPS) as an adsorbent surface to remove Cu (II) and Pb (II) from synthetic solutions. The equilibrium adsorption data of Cu (II) and Pb (II) on DPS was the best fit for Langmuir isotherm. Monolayer capacities were 17.29 and 53.02 mg / g respectively [37].

(Abd Ali et al., 2016), Studied adsorption of Cu (II) and Cd (II) ions from wastewater by eggshell as an adsorbent surface. Thermodynamic factors showed that adsorption was spontaneous in common conditions and endothermic. Adsorption followed pseudo second order [38].

(Farhan et al., 2016), Studied adsorption of Zn (II) ions from wastewater by malvaparviflora as an adsorbent surface. The experimental results showed that greatest removal of Zn (II) was at PH = 2. Adsorption data fits well to pseudo first order [39].

(Kareem, 2016), Studied removal of Cr (VI) ions from synthetic solutions using olive leaves as an adsorbent surface. Effect of adsorbent quantity, pH, Cr (VI) concentration, contact time, particle size, and mixing speed on olive leaf removal effectiveness were investigated using batch experiments. Adsorption data fits well with the Langmuir adsorption isotherm model[40].

(Ahmed N. Abd et al. 2017), Investigated the removal of metals from sewage water using Attapulgite clay. The experimental results showed that concentrations of metals were (Fe =20, Pb = 2, Ni = 3, Zn = 7, Co = 7, Cu = 2, Cd = 0.1 and Cr = 4} mg/L, and decreased after treatment to {Fe = 1.15, Pb = 0.285, Ni= 0.37, Zn = 0.86, Co = 0.3, Cu = 1.2, Cd = 0.07 and Cr = 1.1) mg/L[41].

(Hammood, 2017), Studied adsorption of Cu (II) ion from wastewater by spent tea paper as an adsorbent surface. The experimental results revealed that the maximum amount of Cu (II) removed was approximately 99.8%, the isotherm adsorption fits well with the Langmuir isotherm, and kinetic data fit with Lagergren's first order model [42].

(Saed and Jaleel, 2017), Studied removal of Cu (II) ions from synthetic solutions by modified and original papyrus as an adsorbent surface. The experimental results demonstrated that after dealing with thiurea and urea, results increased from 56% removal by normal cane to 61% removal by urea modified and 68% removal by thiurea modified. The adsorption process fit with Langmuir and Freundlich adsorption isotherms, and kinetic factors were pseudo second order fitted[43].

(Wang et al., 2018), Studied adsorption of Cu (II) and Cd (II) from wastewater by Attapulgite (ATP) encapsulated by Sodium Alginate (SA) as an adsorbent surface. SA-prepared adsorbents had a maximum adsorption capacity of 119.0 mg / g for Cu (II) and 160.0 mg / g for Cd (II). These adsorbents had high stability and were freely recyclable, caused by their floatability in water[44].

(Nefzi et al., 2018), Investigated adsorption of Cu (II) and Ni (II) ions from synthetic solutions by palygorskite and diatomite clays. Results exhibited that greatest adsorption on diatomite clay was 78.44% for Cu (II) at pH = 4 and 77.3% for Ni (II) at pH = 7, whereas greatest adsorption on palygorskite was 91% for Cu (II) and 87.05% for Ni (II) in similar conditions, and adsorption process was fit to Freundlich and Langmuir isotherms. A pseudo second order model can be used to represent it[45].

(Kausar et al., 2018), Studied removal of Cr (VI) ion from synthetic solutions by a new type of composite Attapulgite-melamine-urea (AMU) as an adsorbent surface. The studies indicated that the adsorption was able to remove the Cr (VI) ions at adsorbent mass (2 g), pH = 2, contact time (90) min. and temperature (298)K. The adsorption process fits well with the Freundlich isotherms [46].

(Khan et al., 2019), Studied removal of Cd (II) and Ni (II) ions from synthetic solutions of normal clay minerals from southern Saudi Arabia. According to the results of the experiment, 1.2 g of clay was enough to remove 99.5% of Ni (II) and 97.5% of Cd (II) from a 40 mg / L synthetic solution, with the greatest adsorption capacity of clay for Cd (II) and Ni (II) ions being (3.3 and 2.7) mg / g, respectively. Results approve the role of natural clay as a cheap, environmentally friendly and healthy natural adsorbent substance in waste water treatment processes[47].

(Mnasri-Ghnimi and Frini-Srasra, 2019), Investigated removal of Cd (II), Co (II), and Cu (II) ions from water by mixing pillared and single clays as adsorbent surfaces. A study of Cd (II), Co (II), and Cu (II) adsorption on natural clays and pillared clays exhibited that pillared clays had the greatest adsorption capacity compared to unpillated clays. Adsorption fitted to second-order kinetics, and Langmuir exhibited good fits to experimental results[48].

(Es-Sahbany et al., 2019), Studied removal of Ni (II) ions from wastewater by natural clays from the Ain Dorrij-Ouezzane region of Morocco. The experimental data exhibited that rate of nickel removal is 70-

75% in the range of time between (30 to130) minutes according to the linear forms of the isothermal models (Langmuir and Freundlich) [49].

(Kakaei et al., 2019), Investigated Pb (II), Co (II), and Zn (II) ions adsorption using new clay modified with triazole and triazolium ligands. The adsorption efficiency of these materials has been determined using related models like Freundlich and Langmuir, and also by kinetic models. Such adsorbents have been more active in the adsorption of metal ions[50].

(Abdulateef et al., 2020), Studied treatment of sewage water in the chemistry department – college of science in Diyala University, which is located in the north east of Baghdad City in Iraq, using local Attapulgite clays before disposing them into the environment. This study includes the use of attapulgite clay to decrease proportion of metals ions (Cr, Co, Cd, Cu, Mn) and suspended solids (SS) in sewage water [51].

1.3 Aim of study

1- Removal of Cr (III), Cu (II), and Zn (II) ions from the industrial wastewater sample of Al-Quds power station using Attaplugite and Flint clays as inexpensive, readily available, and environmentally friendly adsorbent surfaces.

2-Determine the optimum conditions for adsorption of Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clays from synthetic solutions in mono-system using batch techniques such as temperature, clay dosage, contact time, and solution pH.

3- Adsorption models study by Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherms to study and understand adsorption behaviors.

4-Thermodynamics investigation of adsorption processes of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint clays, as well as the kinetics of the adsorption process.

Chapter Two

(Theoretical Part)

2.1 Adsorption

Adsorption takes place as a result of interactions between adsorbate molecules and the surface of the adsorbent. Adsorption uptake by the adsorbent is heavily influenced by its surface properties, such as surface area and pore volume. Throughout the adsorption process, adsorbate molecules encircle the active sites of porous adsorbents that have a predetermined level of energy. According to IUPAC, adsorbent energy sites are classified into three pores sizes, namely micro-pores 2 nm, meso-pores (2 to 50) nm, and macro-pores > 50 nm [52].

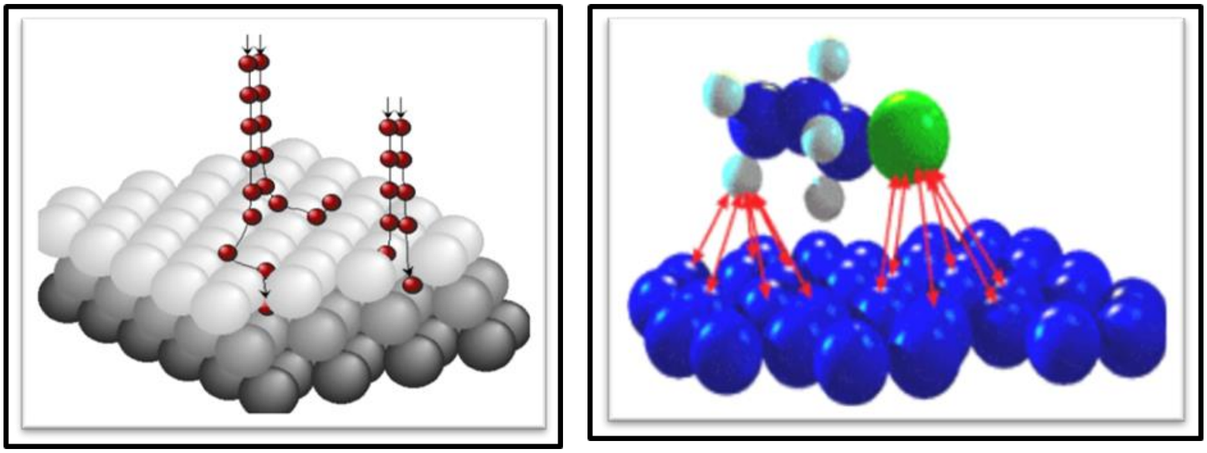
Adsorption is among the most commonly used techniques in wastewater treatment because of its major benefits, cheap cost, simple design, high efficiency, and ease of maintenance[53]. The adsorbate is the solute that participates in the adsorption process such as heavy metals, and the adsorbent is the material that provides the surface such as clay[54].

2.1.1 Adsorption types

Physical and chemical adsorption are the two types of adsorption [55].

1- Physical adsorption is caused by the interaction of intermolecular forces (van der Waals forces), such as adsorption of gas by activated carbon. Physical adsorption is typically performed at a low temperature, low adsorption heat, fast adsorption rate, and is nonselective. Because the effect of intermolecular attractions are weak, changing the structure of adsorbate molecules is difficult, separating adsorbed material is simple, and the energy of adsorption is low(also called physisorption). As shown in Fig.(2.1(a)).

2- Chemical adsorption leads to the creation and destruction of chemical bonds. The adsorption heat of uptake or release is greater, as is the activation energy required (also called chemisorption). Chemical adsorption and physical adsorption are not separated and frequently occur together. In technology of wastewater treatment, many of adsorption is the cause of several types of adsorption processes, Because the effect of adsorbents, adsorbates, and other factors, a few other types of adsorption may take the lead. As shown in Fig.(2.1(b)).

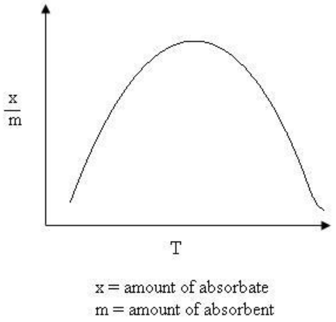
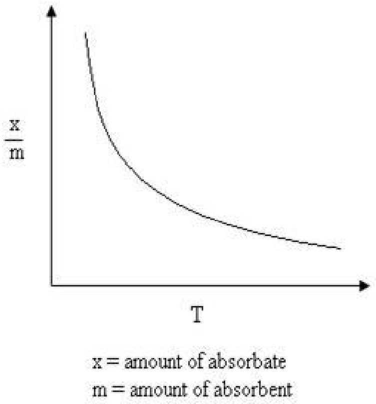


(a.) Physical adsorption

(b.) Chemical adsorption

Fig. (2.1) Chemical and physical adsorption [56].

Table (2.1) comparison between chemisorption and physisorption[57].

Item	Chemisorption	Physisorption
Adsorption force	Strong (chemical bond)	Weak (van der waal)
Adsorption layers	Single layer	Single or multiple layers
Adsorption rate	low	fast
Selectivity	selective adsorption	Nonselective adsorption
Adsorption heat	High	Low
stability	stable	instable
Activation energy	High	Low
		

2.1.2 Adsorption mechanism

Adsorption happens in three stages. The adsorbate spreads from main body of flow to adsorbent particle's outside surface in first step. Adsorbate then travels from small region of outer side to pores in each adsorbate molecules in the second step. Because these pores have the most available surface area, the majority of adsorption takes place in them. Finally, the contaminant particle adheres to the pore's surface[57]. As shown in Fig.(2.2).

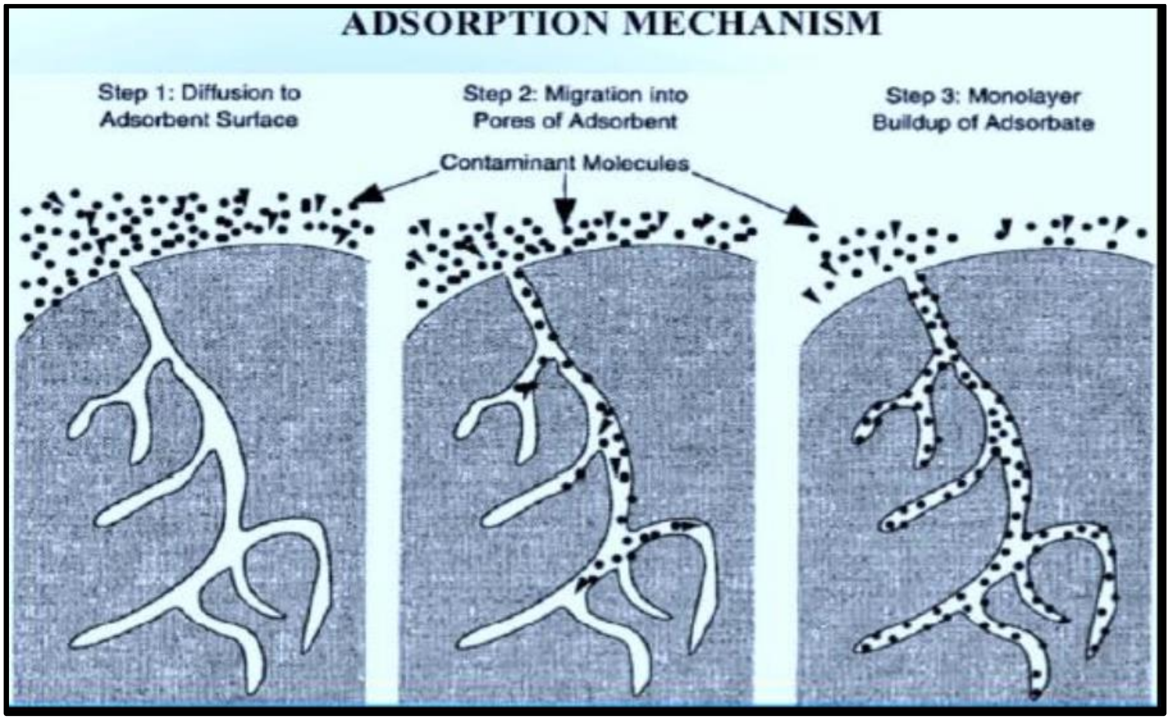


Fig.(2.2) Mechanism of Adsorption[58].

2.1.3 Factors affecting the adsorption process

2.1.3.1 Temperature effect

Temperature is also an important factor. Adsorption is generally exothermic; it is just an analysis of temperature dependency on adsorption interactions that gives knowledge about entropy and enthalpy changes throughout adsorption; consequently, a decrease in temperature leads to an increase in adsorption. On the other side, optimizing adsorption with increasing temperature indicates that process endothermic.

The amount adsorbed in chemisorption may increase or decrease with increasing temperature dependent on kind of reaction and bonding between adsorbed and surface, whereas in physisorption, a decrease in temperature increases the adsorption extent[57,59,60].

2.1.3.2 Effect of pH

The influence of change of pH on adsorption capacity is caused by the adsorbent's surface charge distribution, that can be altered. Furthermore, changes in the pH of the solution have a significant influence on the amount of adsorption due to their effects on the adsorbent, chemical state of the solvent, and the adsorbate. The competition for (H^{+1}) and (OH^{-1}) ions, as well as their overlapping with the adsorbate, adsorbent surface, or solvent, can be used to demonstrate this effect. The grade of ionization of a types is affected by pH (e.g., a weak acid or a weak base). This has an influence on adsorption. According to the adsorbate functional groups, the varying adsorption extent either increases, decreases, or remains constant[60].

2.1.3.3 Adsorbate nature effect.

The size, shape, presence of polar groups, and concentration of the adsorbate material all affect the reaction between adsorbent surface and the adsorbate molecules. The adsorption process can be selective of one of the components with the increase in molecular weight and solubility of polar group and charges the interference between the surface adsorbent and adsorbate molecules [61].

2.1.3.4 Adsorbent nature effect.

Adsorption is affected by the chemical nature of the surface, such as the surface area, adsorbent surface, and volume of adsorbent molecules dispersed on the surface[62]. The chemical structure of functional groups, solid surface adsorption rises as particle volume decreases and surface area increases. An increase in active sites means more adsorption capacity [63].

2.1.3.5 Effect solubility of solute (adsorbate) in liquid.

Substances with high solubility in water will be harder removed from substances slightly soluble (i.e., adsorbed). Also, polar substances (they have greater affinity for water) will be removed more than non-polar substances [57].

2.1.3.6 Contact time effect

The adsorption processes are influenced by contact time, where time needed for adsorption systems to achieve equilibrium differs depending on surface nature and unfilled adsorption sites[64]. It is the longest period of time when adsorption process is finished and the equilibrium or change is minor [65,66].

2.1.3.7 Ionic strength effect

The neutral molecules are adsorbed to a larger degree than more highly ionized molecules[57]. Soluble electrolytes typically exhibit their action by influencing adsorbate solubility or physical properties[67] (surface potential and surface charge)[68]. When electrolyte used to increase ionic strength is also more soluble in solvent than adsorbate, ionic strength increases the extent of adsorption[67].

2.1.4 Adsorption from solutions

Adsorption from solution upon adsorbent of solid is a fairly complicated matter; it varies from adsorption of single materials (vapors, pure liquids ,and gases) in where the solution includes at least two components that form a crowded surface layer. Solvent particles start competing with solute particles for access to the surface's active sites. As a consequence, when the solution concentration changes, the solution components dislodge one another. That is a characteristic of adsorption from solution. Because the function of the solvent is becoming clear, this process is more resistant to treatment theoretically than treatment of gas in a solid process. The nature of solute-solvent interactions in the solution phase and inter - facial area, as well as their interactions with adsorbent, also influences this process[56,67].

Adsorption by a porous adsorbent from a solution occurs in four stages [69]:

(a.) Solute molecules travel from the solution bulk to the adsorbent's outer surface.

(b.) Solute molecules migration across the interaction and adsorption on outer surface sites.

(c.) Solute molecules migration inside adsorbent's pores , and

(d.) Solute molecules interact with unfilled active sites on inner surface, bounding pore and capillary areas of adsorbent.

Single or more of preceding steps may govern the quantity of solute adsorbed on the solid material.

2.1.5 Adsorption isotherms

The equilibrium distribution of particles between two phases, which may be liquid, gas, or solid, is among the foundations for adsorption [70]. The adsorption isotherm is the differences in the adsorption capacity as a job of adsorbate's equilibrium concentration at a constant temperature [71].

Adsorption isotherm can be graphically represented by plotting the adsorbate quantity on the solid surface (q_e (mg/g)) against the concentration of adsorbated in solution (C_e (mg/L)) at equilibrium[72].

There is a wide range of adsorption isotherm forms for chemisorption, with an primary sharply increasing curve that steadily flattens. The initial increase is related to the surface's greater trend to bind the adsorbed particles, and the adjustment off is related to the saturation of these forces. On the other hand, physical adsorption is characterized by an adsorption isotherm that appears to have a progressively positive slope with rising adsorbed concentration (for adsorption from solute) and gas pressure (for gas adsorption)[72]. Giles and colleagues classed the various isotherms of adsorption from solution on solid active surfaces as shown in Figure (2.3).

Giles classified isotherms into four major groups based on the initial segment plotted when the solution is quite dilute (S, L, H, and C). Depending on the rise in solute concentration, these classes have subclasses (1, 2, 3, 4, and max). Giles attempted to decipher the adsorption mechanism, as well as the direction of the adsorbed molecules and other adsorption-related factors. Giles drew the following shapes to demonstrate his point:

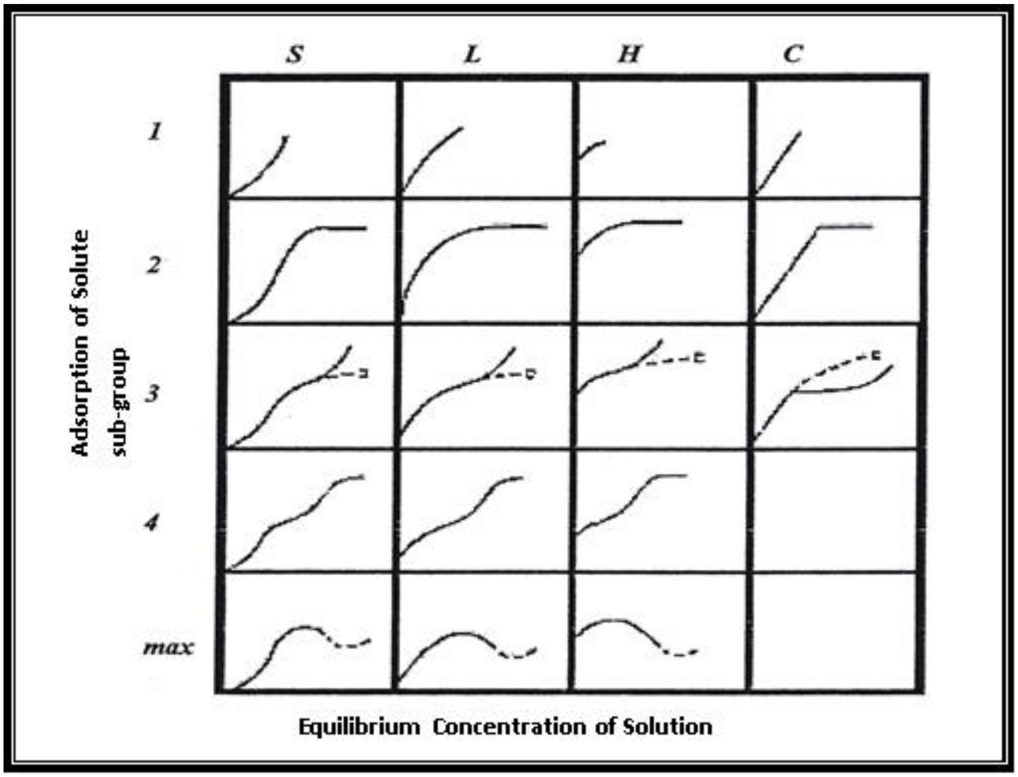


Fig.(2.3) Giles classification adsorption isotherm [73].

S-shapes indicate that the adsorbed layer is vertical or flat, that here strong inter-molecular attraction inside adsorbed layer, and that adsorbate is mono-functional.

L-shapes are formed when the sites are few and broadly separated, resulting in monolayer adsorption, and this type is referred to as simple Langmuir isotherms, which are suggestive of particles adsorbed flat on a surface, such as the cyclic hydrocarbons or carbon series.

H-shapes are obtained if here a great adsorption affinity, such as in situation of great molecular weight composites such as polymers and proteins, and this isotherm can also be noted even when solution is quite dilute.

C-shapes are constant-barrier linear curves produced via materials that enter the adsorbent more easily and quickly than solvent [73,74,75].

2.1.6 Adsorption theories

Adsorption equilibrium results are typically defined by adsorption isotherms, that are critical for optimizing adsorption process design parameters. They are indeed useful in providing enough physical and chemical data to know the adsorption mechanism. These isotherms connect to the quantity of solute adsorbed at equilibrium per mass of adsorbent, q_e, to a concentration of adsorbate at equilibrium, C_e. To fit experimental data in this study, three main isotherm models were chosen: Langmuir, Freundlich, and Dubinin–Radushkevich (D–R).

2.1.6.1 Langmuir isotherm

Langmuir isotherm explains monolayer adsorption under the assumption that all adsorption sites provide equal adsorbate affinities (the surface is homogeneous) so this adsorption at one site has no effect on adsorption at another [76].

The equation for the Langmuir isotherm is as follows [77]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad \ldots 2.1$$

Where q_e represents the quantity of adsorbed for unit weight of adsorbent (mg / g), C_e represents equilibrium concentration of adsorbate (mg / L), q_{max} represents adsorption capacity (mg / g), or monolayer capacity, and K_L represents the Langmuir equilibrium constant related to energy of adsorption and binding site affinity (L / mg) [78].

The following are the linear forms of the Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad \ldots 2.2$$

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \qquad \ldots 2.3$$

$$\frac{1}{q_e} = K_L q_{max} - K_L q_e \qquad \ldots 2.4$$

The slope and intercept of linear plot of experimental results of C_e/q_e vs C_e, equation (2.2), or the slope and intercept of linear plot of experimental results of $1/q_e$ vs $1/C_e$, equation 2.3, can be used to calculate the values of q_{max} and K_L.

One of key traits of Langmuir model could be described in term of the dimensionless constant known as the equilibrium factor R_L, which is described as [79]:

$$\boldsymbol{R_L = \frac{1}{1 + K_L C_0}} \qquad \ldots \mathbf{2.5}$$

Where C_o represents initial concentration in (mg / L). Value of R_L suggests whether isotherm is unfavorable adsorption (R_L > 1), linear adsorption (R_L = 1), favorable adsorption (0< R_L <1), or irreversible adsorption (R_L =0) [80].

The linear form to linearize experimental results by plotting $C_{\mathbf{e}}/q_{\mathbf{e}}$ against $C_{\mathbf{e}}$. The slope =($1/q_{max}$) and intercept =($1/K_Lq_{max}$) of the linear equation are used to calculate the Langmuir constants q_{max} and K_L [81]. As shown in Fig.(2.4).

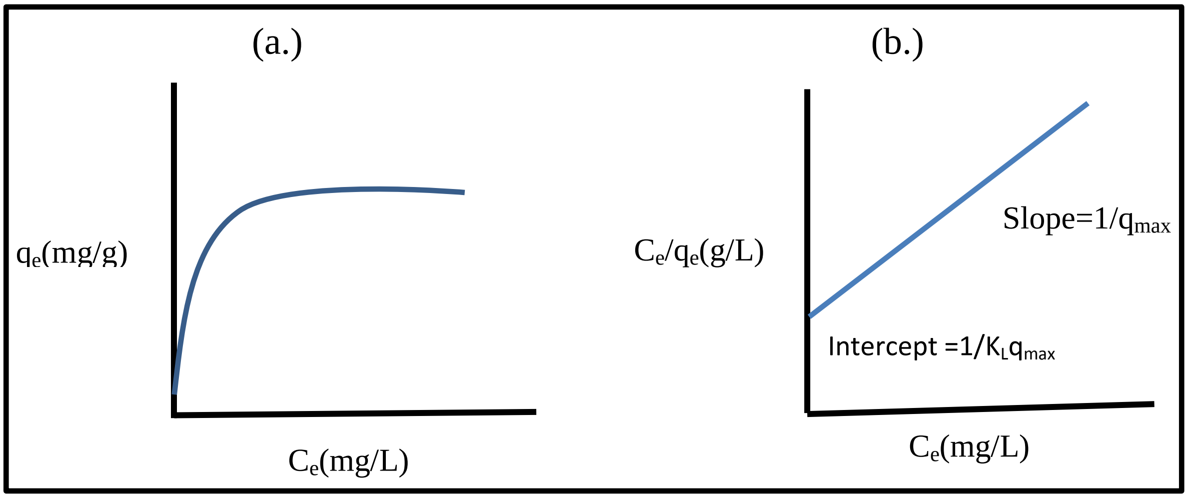


Fig. (2.4) (a.)The Langmuir isotherm (b.) The Langmuir isotherm in linear form.

2.1.6.2 Freunlich isotherm

Freundlich isotherm is a common relationship used to describe the sorption equation. It is concerned with heterogeneous adsorption on surfaces and the interaction of adsorbate molecules. The Freundlich equation predicts that the sorption energy decreases exponentially as an adsorbent of the sorption centers is completed. It is used to explain heterogeneous systems and is expressed by below equations [82,83].

$$q_e = K_F C_e^{\frac{1}{n}} \qquad \dots 2.6$$

Where K_F represents capacity factor or experimental Freundlich constant (mg/g), (1/n) represents heterogeneity factor. By taking logarithms of equation (2.6), the Freundlich linear form can also be completed.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \dots 2.7$$

The intercept = log K_F and the slope = (1/n) have been calculated using the log q_e vs log C_e plot. As shown in Fig.(2.5).

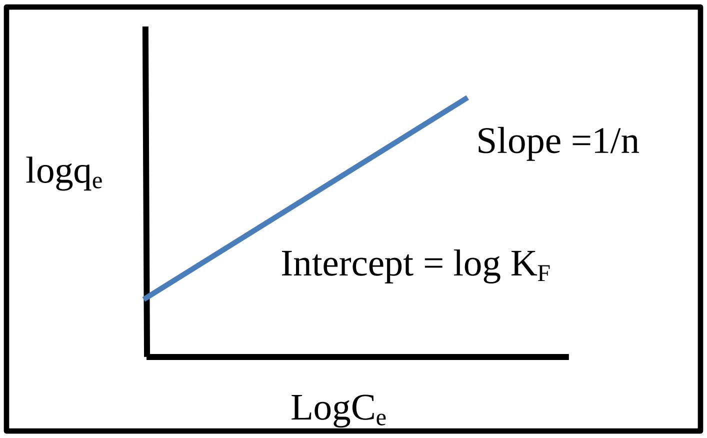


Fig.(2.5) The Freundlich isotherm in linear form.

The constants (K_F and n) are linked to the strength and distribution of the adsorptive bond, respectively[82]. Mathematically, it has been indicated that n can be classified as an indicator of adsorption site heterogeneity. For example, as n approaches zero, surface sites heterogeneity increases [84,85]. When n is greater than one, bond energies raise with surface density, when n is less than one, bond energies reduce with surface density, and when n equals one, all surface sites are equivalent[82].

2.1.6.3 The Dubinin-Radushkevitch (D-R) isotherms

Dubinin-Radushkevitch (D-R) model, that was first suggested as an observed adjustment of a Polanyi adsorption potential theory, was the fundamental equation for describing quantitative adsorption of gasses by micro-porous sorbents. Based on the idea that adsorption mechanism in micro pores is pore-filling instead of layer-by-layer surface coverage. The equation usually applies good to adsorption processes containing only van der Waals forces and is particularly important in describing adsorption on activated carbon. This isotherm appears to be more common than the Langmuir isotherm because it does not assume a constant sorption potential or a homogeneous surface. [86,87]. The D-R equation is [88].

$$\ln q_e = \ln q_{max} - \beta\varepsilon^2 \qquad \ldots 2.8$$

where q_e (mg/g) represents adsorbate amount at equilibrium, q_{max} (mg/g) represents D-R monolayer capacity, β (mol^2/KJ^2) represents a constant connected to the sorption energy. (ε) represents Polanyi potential that is connected to the concentration at equilibrium as equation (2.9)[86].

$$\varepsilon = RT\,ln\left(1 + \frac{1}{C_e}\right) \qquad \ldots 2.9$$

The following relation is used to determine the main energy of sorption (E).

$$\boldsymbol{E} = (-2\boldsymbol{\beta})^{-0.5} \qquad \ldots \mathbf{2.10}$$

The sorption energy (E) value provides data about kind of adsorption process, whether physical or chemical. If this value is larger than 16 kJ mol^{-1}, adsorption type is chemical, whereas if this value is less than 16 kJ mol^{-1}, the adsorption type is physical **[87,89]**. By using the plot of ln q_e versus (ε^2) can be calculated adsorption energy constants (β) and main adsorption energy **[87,89]**. As shown in Fig.(2.6).

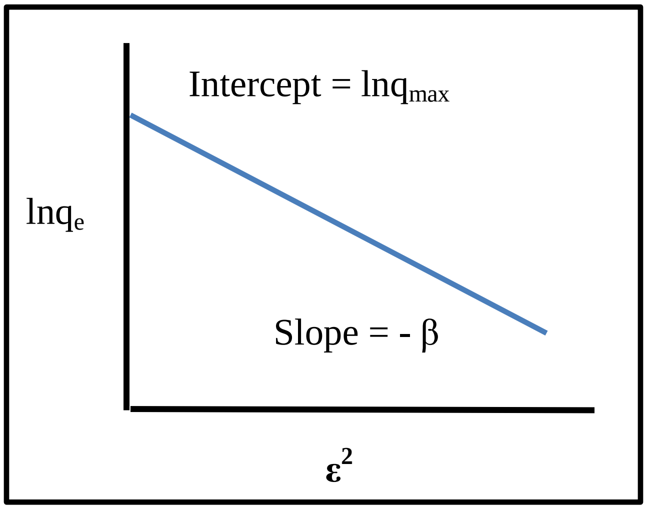


Fig.(2.6) The D-R isotherm in linear form.

2.1.7 Thermodynamics of adsorption

Adsorption thermodynamic procedure yields great insights about bond strength magnitude, spontaneity, and randomness in the adsorption process [90]. The assessment of heat effects associated with adsorption is among the most important jobs of adsorption thermodynamics [91]. The adsorption heat from a solution is typically many times lower than the adsorption heat from a gaseous on a certain adsorbent. The heat change that happens when a solution interacts with a solid is more difficult to reflect than the heat change that happens when a single gas is adsorbed by a solid[92]. Adsorption isotherms at various temperatures in reversible systems can be used to assess the thermodynamic functions that describe adsorption from solution [93].

The assessment of differences in solution density and solubility of materials with temperature is evidently a necessary condition of adsorption processes at various temperatures (that leads to the analysis of thermodynamic results and their explanation)[91]. Changes in thermodynamic parameters including such free energy (ΔG°) KJ. mol^{-1}, enthalpy (ΔH°) KJ. mol^{-1}, and entropy (ΔS°) J. K^{-1} mol^{-1} are calculated as follows:

The Van't Hoff equation indicates the adsorption equilibrium constant, K, thermodynamically as [94].

$$\ln K = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \qquad \ldots 2.11$$

At various temperatures, the adsorption equilibrium constant, K, is also calculated and is described as the following equation[94]:

$$\lim_{q_e \to 0} \frac{q_e}{C_e} = K \qquad \ldots 2.12$$

The intercept of plotting ln q_e / C_e vs q_e yields K values. In addition, The adsorption processes equilibrium constant (K) can also be calculated using the following equation[95].

$$\boldsymbol{K = 1000K_L \times M.Wt\ of\ adsorbate \times 55.56} \quad \ldots \mathbf{2.13}$$

where K_L represents Langmuir constant and (55.56) represents water concentration in solution. The following relationship is used to calculate Gibbs free energy changes (ΔG°) for reactions[94]:

$$\boldsymbol{\Delta G^\circ = -RT \ln K} \qquad \ldots \mathbf{2.14}$$

$$\boldsymbol{\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ} \qquad \ldots \mathbf{2.15}$$

Whereas (R) ($8.314.J.mol^{-1}K^{-1}$) denotes gas constant and T (K) denotes temperature. Thus, the thermodynamic factors ΔH° and (ΔS°) can be calculated using Van′t Hoff equation (2.11) from the intercept and slope of a plot of ln K vs. (1/T), which produces a straight line.

2.2 clays

Clay is described as a naturally produced sediment made up of one or more mineral and secondary compounds[96]. It is mainly composed of iron, hydrated silicates of aluminum, or magnesium. When clays are adequately crushed and washed, hydrated alumina or iron oxide play a large role in colloidal or near-colloidal particles, which leads to plasticity. Clays are distinguished from many other soil particles by their plasticity. Because of its porosity, clay has a large surface area, resulting in the most adsorptive action[97].

Clays are fantastic adsorbent substances due to their mechanical and chemical stability, large specific surface area, layered structure, high cation exchange capacity, and other characteristics. Clays carry a main role in many fields by acting as a healthy scavenger of contaminants by absorbing anions and cations via ion adsorption, exchange, or both. As a result, clay usually contains substitutable cations and anions that are carried onto the surface. Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, H^+, K^+, PO_4^{-3}, Cl^{-1}, SO_4^{-2},, and NO_3 are the most common cations and anions located on clay surfaces [98,99].

2.2.1 Attapulgite clay

Attapulgite is a silicate sequential category clay metal. It gets its name from the city of Attapulgius in Florida, USA.$[[(OH_2)_4(Mg.Al)_5(OH)_2Si_8O_{20}]4H_2O]$ is its chemical formula. This involves a group of clay series, of which Attapulgite is a member[100,101]. Fiber grains in Attapulgite include channels that run along the crystal structure. In its natural state, raw metal contains water. Thus, thermo treatment means absorbing all of the water in these channels and preparing them to accept new molecules. Attapulgite has a high adsorption efficiency because of this feature[102]. This metal's structure consists of tetra connections in the shape of double chains. Aluminum or Magnesium atoms link these chains, with each atom encircled by six Oxygen atoms[100].

Attapulgite clay is a naturally occurring mineral with a porosity and a large surface area. It has a special features which qualified it to use in certain regions [103,104]. The structure of Attapulgite is defined by the term chain layer. It is a unique mineral structure in which alumino–silicate layers form strips that are joined at the edges.

Attapulgite crystals are needle-shaped (circular) rather than flat or flake-like, and have a high surface area [105]. Attapulgite is superior to kaoliniteels because it has an open structure that encloses a channel into that organic compounds [106]. It also has a small trimorphic unit with a character that is middle between di and tri octahedral. Historically, such minerals were categorized as (chain - lattice silicates). However, they are linked to phyllosilicates rather than chain silicates [107]. Attapulgite forms in a variety of environments, including salty water lakes and sea depositions, as well as evaporation-heavy basins. Attapulgite can be found in Iraq's western desert and in Najaf. It is greyish in color and does not dissolve in water, hydroxyl basic solutions, or organic acids. Iraqi Attapulgite clays were found to be effective in removing the color of paraffin wax in tests. And it is used in adsorption in a wide range of industrial and medical fields [100,101]. Figures (2.7-2.9) show the crystal structure, tetrahedral layer, and octahedral layer of Attapulgite clay's structural composition.

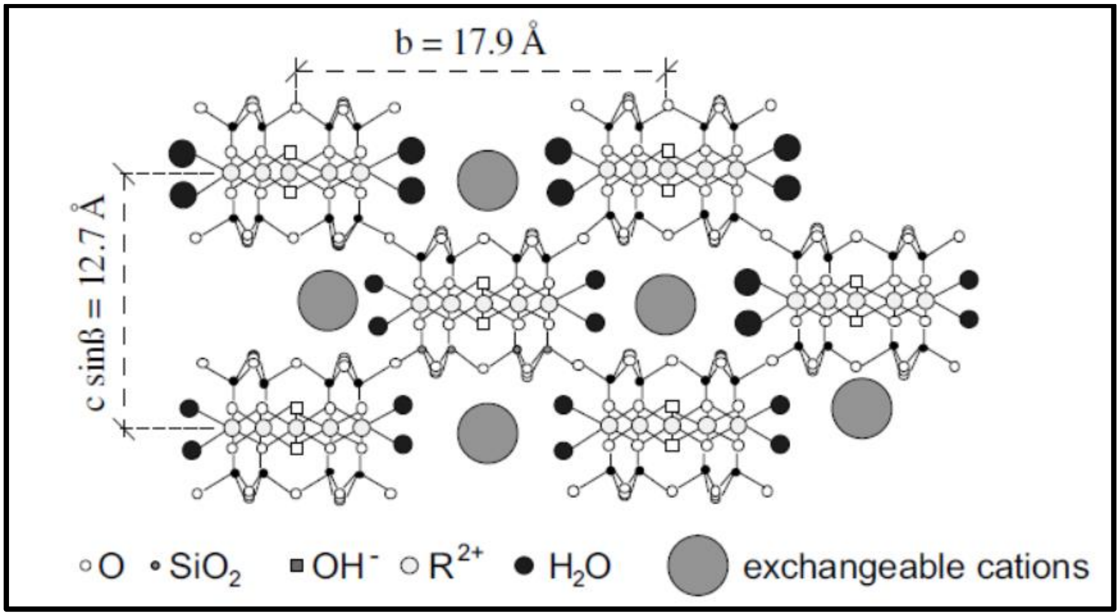


Fig. (2.7) The Crystal Structure of Attapulgite clay [108] .

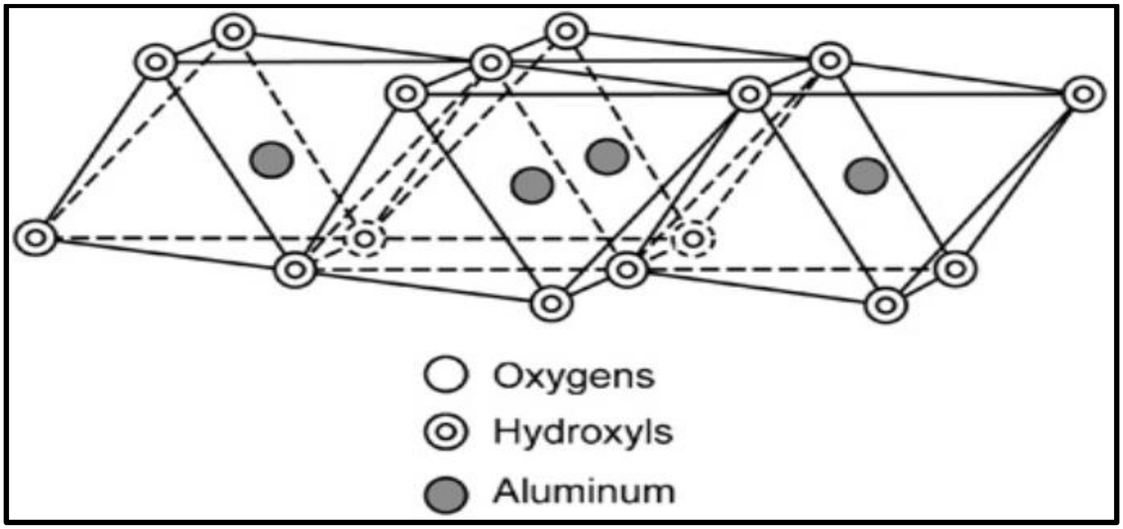


Fig. (2.8) an octahedral layer for the structural composition of Attapulgite clay [108].

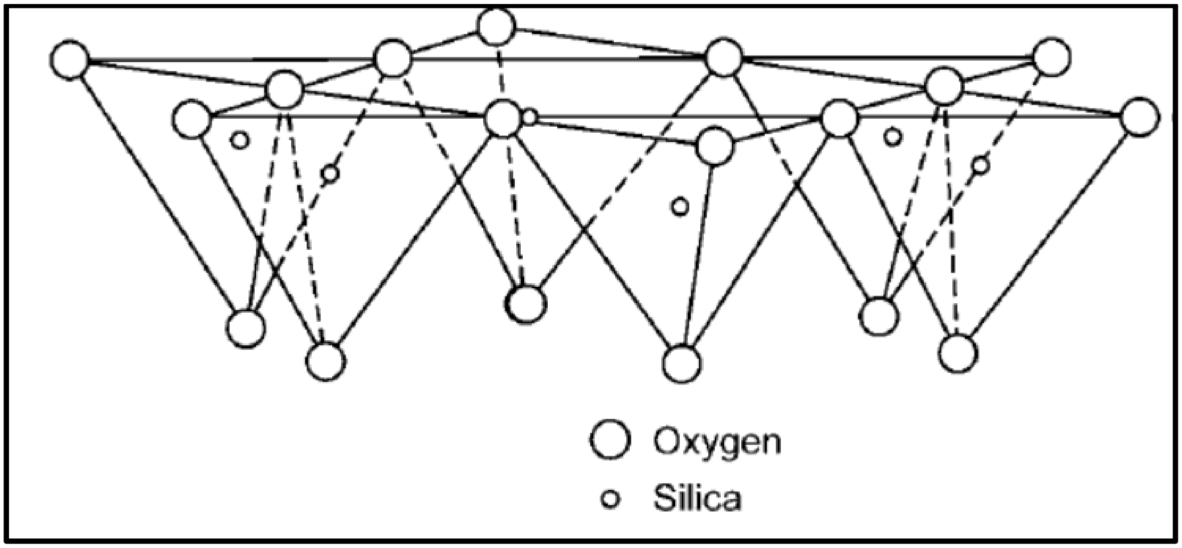


Fig. (2.9) a tetrahedral layer for the structural composition of Attapulgite clay [108].

2.2.2 Flint clay

The Flint is a main formula of silica, and is used in the production of white clay shapes and in the porcelain industrial sector. It is made up of small quartz crystals that are linked together by water molecules and has a specific weight of (2.62) less than quartz. Flint is often more efficient than quartz, and it contributes to the white color of burned shapes caused by organic matter combustion[109]. It governs the thermal expansion of the burned particles. Caolines $Al_2Si_2O_5(OH)_4$ is the major clay metal in flint clay, accounting for 83.3 percent of the total weight. Flint clays differ from many other caoline clays in that they have sharp angles, are rigid, resist decay in water, have an oily feel, and occasionally include nodes. Its solid form is due to the formation of free silica from the interlocking of caoline grains with one another. In terms of appearance, the name "Fint clay" is very suitable because it has a dense, compact, comparatively hard structure that breaks with a sharp, conchoidal structure which is like Flint[12].

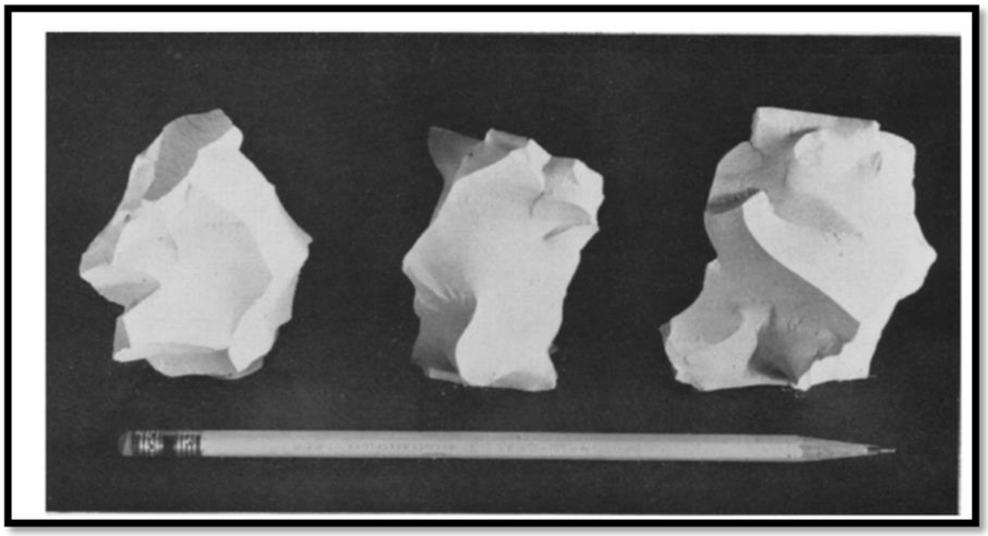


Fig.(2.10) The structure of resembles Flint [110].

2.3. Heavy metals

Heavy metals are the most essential aspects in this study. Heavy metals are metals with an atomic density of 5g/cm^3 or higher, which include metals from periodic table groups IIA, IIIB, IVB, VB and VIB. Heavy metals are defined as metals in the periodic table with an atomic number greater than 20, with the exception of alkali metals[111]. This is because their environmental behavior and chemical properties are so similar. Most of them seem to be trace metals found in the earth's crust, and the vast majority of them are toxic even in trace amounts.

Heavy metals are harmful and. dangerous to humans and plants. Zinc, for example, is required for human growth. If large amounts are consumed or breathed, they all are poisonous. The major problem with heavy metals is bioaccumulation as a result of long residence times[112].

Metals are present in rocks and are released into the environment (soil, water, and air) as a result of human activity or naturally. Metals such as (Cu, Zn, Pb, Ni, Cd, and Hg) can be identified as divalent cations in wastewater and several natural soils, whereas (Cr and As) can be discovered in varying oxidation states[113,114].

2.3.1 Heavy metals in industrial wastewater

Heavy metals such as copper, chromium, zinc, lead, cadmium, and others are frequently found in industrial wastewater, and their release into the environment represents a risk due to the toxic effects they have on terrestrial and marine life, including humans. Heavy metals are present in several processes, including battery manufacturing, smelting, mining, and plating, as well as municipal and industrial wastewater discharge[115].

Industrial wastewater is defined as wastewater generated by any processing, institutional, manufacturing, agricultural, or commercial process, as well as any operation that emits wastewater other than sanitation or household wastewater[65]. Organic and inorganic chemical pollutants can be found in industrial wastewater. Organic include fats, carbohydrates. and protein . Inorganic include nitrites, free ammonia, nitrates, organic nitrogen and trace minerals like heavy metals. As industrial revolution progresses, more heavy metals are being discharged into the environment, triggering scientists to evaluate methods for economically and efficiently treating heavy metal-bearing wastewaters[116].

2.3.2 Heavy metals treatment

The vast majority of heavy metal salts are water soluble and form aqueous solutions. As a result, it cannot be removed using conventional physical methods. That's clearly more noticeable if the heavy metal concentration in the water is low, such as (1-100) mg dissolved metal ions for every liter. There are various methods available today for removing heavy metals from wastewater. There are six major methods: reverse osmosis, adsorption, electrochemical, biological treatment, membrane filtration, and in situ water treatment[117]. Most of these methods have limitations, such as consumption of energy, inefficient removing contaminants , and the creation of a secondary waste material, toxic slag, which would necessitate additional special support[118,119]. One of the most effective methods for removing heavy metals from water is adsorption, which is a low-cost method of water purification due to its efficiency, ease of use, and versatility. This method is considered as a global water treatment and purification method because it can be used to remove inorganic, organic, and biological contaminants that are soluble and insoluble in water, and it has a 99% removal rate[120].

2.3.3 Heavy metals under study

2.3.3.1 Chromium

Chromium is a chemical element that can be observed in soil, rocks, plants and animals. It appears in the environment in a variety of forms depending on pH. The most famous form is chromium (III), which is an important mineral that aids the body's consumption of sugar, fat, and protein. Chrome plating, leather tanning, wood preservation , and color pigments all use chromium. Chromium (III) and chromium (VI) are the most common forms of chromium that enter the soil, water, and air. Because chromium is forcely connected to the soil, only tiny quantities can also dissolve in the water, and thus it doesn't quite reach the underground water in bigger quantities[62]. Eating or breathing excessive amounts of chromium can cause stomach ache, difficulty breathing, liver or kidney damage, and may be death. Chromium is a known carcinogen[121,122].

2.3.3.2 Copper

Copper is commonly present in large amounts in wastewater as it's the most useful and widely used metal in a wide range of industries, including electroplating, metal finishing,etching, and plastics[123]. Copper is a trace metal that humans require for its job in growth of bone and tissue and enzyme synthesis[124]. However, if copper ingested in large quantities, it becomes toxic and carcinogenic. This may cause liver and kidney failure, and vomiting. Undefined outcomes include diarrhea, tachycardia, abdominal pain, nausea, gastrointestinal bleeding, hemolytic anemia, respiratory difficulties, and death[125].

2.3.3.3 Zinc

Zinc products are generally used for the manufacturing of rubber, paint, wood preservatives, and dyes. Zinc solubility varies greatly based upon the compound; for instance, zinc phosphate is insoluble while zinc nitrate is highly soluble. Many zinc compounds can contaminate rivers, groundwater, streams and lakes depending on soil type[126]. Zinc levels are critical for good nutrition. A lack of zinc can cause a loss of appetite, fungal infections, sexual immaturity, anxiety, and a loss of taste. The toxic effect usually start at levels (10-15) times greater than what is required for great nutrition, having caused stomach pains, iron deficiency, and variations in cholesterol. Zinc availability decreases with increasing pH in general. Zinc is thought to be highly mobile and bioavailable, and it can accrue in both plants and human foods[112,122].

2.3.4 A brief overview of AAS and ICP-MS

2.3.4.1 Atomic Absorption Spectrophotometers (AAS)

Every element has its own set of electronic energy levels for atoms. This is used in (AAS), where components are absorbed into a flame and switched to free atom vapour. A lamp is pointed at the vapour, that emits light of a certain wavelength.The element will absorb light in their wavelengths.The radiation emitted by a specific energy is deducible. The heavy metal amount can thus be determined in this manner[127].

2.3.4.2 Inductively coupled plasma-mass spectrometry (ICP-MS)

ICP-MS is an analytical technique utilizes by immersing a sample in plasma at a temperature of about 5000K. The samples will dissociate into molecules and ionize into atoms in the plasma. The ions are then moved into a quadrupled mass spectrometer after passing through a cone into vacuum. Ions are sorted by mass in the mass spectrometer and detected with a scanning electron multiplier[127].

Chapter Three

(Experimental Part)

3.1 Apparatus and instruments

The apparatus and instruments used during the study, as well as their details, sources, and location of measurement, are outlined in Table (3.1).

Table(3.1) Apparatus and instruments.

Instruments names	Origins & details	Measurement location
Atomic Absorption Spectrophotometer (AAS)	ShimadzuAA-6200, (Japan)	Instrumental Analysis Lab, Chemical Engineering Department, Engineering College , Tikrit University
Atomic Force Microscope (AFM)	AFM contact mode, AA 3000 SPM 220 V-Angstrom Advanced Inc, Scanning Probe Microscope (USA)	Dr. Abdulkareem M.A.AL-Sammarraie's Lab., Iraq
Shaker Water Bath	BS-11,230 VAC -50 Hz, (Korea)	University of Diyala, Graduate Laboratory, Department of Chemistry Sciences, College of Science
Electric Balance	KERN ACJ/ACS, ACS120-40, WB 12 AE 0308, maximum 120 g, d=0.1 mg (Germany)	
Oven	KERN ACJ/ACS, ACS120-40, WB 12 AE 0308, maximum 120 g, d=0.1 mg (Germany)	
pH Meter	WTW ino Lab PH Meters 7110 Benchtop Meters, PH/Ion (Germany)	
Magnetic Hot Plate Stirrer	ISO LAB Laboratory GmbH, MS-H280-pro (Germany)	
Centrifuge	Type Z200A HERMIE LABORTICHINK, 6000 rpm (Germany)	
Particle size sieve (75 µm)(no.200)	{Germany}	

3.2 Materials used

3.2.1 Chemicals

In the following Table (3.2), The qualities of chemicals used in this project are given:

Table (3.2) Chemicals used

Chemicals	Formula	Purity (%)	Molecular mass(g/mol)	Company
Zinc Chloride	$ZnCl_2$	99	136.286	ROMIL-SA
Chromium nitrate nonahydrate	$Cr(NO_3)_3.9H_2O$	97	400.1483	Alpha chemical
Copper(II)Sulphate pentahydrate	$CuSO4.5H_2O$	99	294.615	Alpha chemical
Hydrochloric cid	HCl	37	36.64	CDH
Sodium ydroxide	NaOH	99	40	Alpha chemical

3.2.2 Adsorbent surfaces

The clays used in this project were provided by the (The General Company for Geological Survey and Mining (GSMGC), Baghdad, Iraq).

3.2.2.1 Attapulgite clay

The main source for Attapulgite clay is an open mine in Iraq's Al-Najaf. Attapulgite is a powder that is greyish buff. It is virtually insoluble in water, organic acids, inorganic acids and alkali hydroxide solutions. Analysis of Attapulgite (Table 3.3) showed several compounds as oxides:

Table (3.3) The chemical analysis of the Attapulgite

Oxide	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**	**L.O.I**	**Total**
% Wt	**41.54**	**10.52**	**5.44**	**15.45**	**4.06**	**l0.17**	**l0.93**	**20.04**	**98.15**

3.2.2.2 Flint clay

The main source of Flint clay is a region in Iraq's western desert. The powder is a greyish white. Analysis of Flint (Table 3.4) showed several compounds as oxides:

Table (3.4) Flint chemical analysis.

Oxide	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**	**L.O.I**	**Total**
% Wt	**45.6**	**35.41**	**l0.69**	**0.2**	**0.1**	**-**	**-**	**13.79**	**95.51**

3.3 Preparation of clays powder

In order to remove soluble substances, Flint and Attapulgite clays were rinsed many times with deionized water, left to dry at (350) K until 5 hours, and left at room temperature(298) K to cool before being contained in sealed containers. The clays have been ground and sieved using sieve of size (no.200) (75 µm) and kept in a closed containers.

3.4 Preparation of industrial wastewater sample

A sample was taken from water contaminated with crude oil used in the fuel washing unit at Al-Quds power station, located northeast of Baghdad. The concentrations of heavy metals under study (chromium, zinc ,and copper) ions were estimated by AAS. The industrial sample was prepared for estimating heavy metal concentrations as the following. 50 mL of the site sample was placed in crystal beaker (100 mL), and 5 mL of (HNO_3 Conc.) was added to it (to digest sample), Placed beaker on a hot plate and leave it heating until it reaches the pre-drying stage. Then added 5 mL of (HNO_3 Conc.) to sample while continuing to heat to obtain a precipitate, then dilute to 25 mL with deionized water and filter through a membrane filter (0.20 µm)**[128]**.

The concentrations of heavy metals were measured by atomic absorption spectrophotometer in instrumental analysis lab, chemical engineering department, engineering college, Tikrit university. Table (3.5) showed the concentrations of heavy metals under study (chromium, copper, and zinc) in industrial wastewater sample.

Table (3.5) The concentrations of heavy metals in industrial wastewater sample.

Date	Conc. of chromium (mg/L)	Conc. of copper (mg/L)	Conc. of Zinc (mg/L)
05/09/2020	76.09	97.39	63.97

3.5 Preparation of solutions used in adsorption process

3.5.1 Standard stock solution of Cr (III) ions

By dissolving (7.933) g of ($Cr(NO_3)_3$ $9H_2O$) in 1 L of deionized water, a standard stock solution of Cr (III) (1000 mg/L) ions was prepared. By diluting the stock solution with deionized water, all solutions were prepared.

3.5.2 Standard stock solution of Cu (II) ions

By dissolving (3.933) g of ($CuSO_4.5H_2O$) in 1 L of deionized water, a standard stock solution of Cu (II) (1000 mg/L) ions was prepared. By diluting the stock solution with deionized water, all solutions were prepared.

3.5.3 Standard stock solution of Zn (II) ions

By dissolving (2.084) g of ($ZnCl_2$) in 1 L of deionized water, a standard stock solution of Zn (II) (1000 mg/L) ions was prepared. By diluting stock solution with deionized water, all solutions were prepared.

3.5.4 Hydrochloric acid

By adding (0.833) ml of HCl(12M) into a (100 mL) flask and dilute it to the mark with deionized water, a solution of HCl (0.1M) was prepared.

3.5.5 Sodium hydroxide

A solution of sodium hydroxide (0.1 M) was prepared by dissolving (0.4g) of NaOH in (100mL) deionized water.

3.6 Batch adsorption process optimization(single system)

Atomic absorption spectrophotometer (AAS) was used to analyze solutions of Cr (III), Cu (II), and Zn (II) ions concentration. The solutions absorbance were determined at ($\lambda_{\mathbf{max}}$ = 324.8) nm for Cu,($\lambda_{\mathbf{max}}$ = 357.9) nm for Chromium, and ($\lambda_{\mathbf{max}}$ = 213.9) nm for Zn.

3.6.1 Effect of contact time

The period that is adequate for adsorption system to reach equilibrium was done according to the procedures in which a volume of (25mL) of an initial concentration (100 mg/L) of Cr (III), Cu (II), and Zn (II) solutions were shaken with (0.05 g) of Attapulgite and (0.3 g) of Flint at a temperature (298K), pH of Cr (III), Cu (II), and Zn (II) ions solutions were (3.8,3.4, and 7.3) respectively (actual pH of the aqueous solution without adjustment), shaking speed was (185) rpm, and the time ranged from (10 to 120) minutes.

At the end of each period, the two phases were separated by centrifuging (5000 rpm, 5min.), then filtered by the filter paper. The metal ions concentration in aqueous state were measured by using an atomic absorption spectrophotometer.

3.6.2 Effect of clay dosage

The effect of clays dosage change on adsorption was investigated in this project by using 25mL of a constant concentration (100 mg/L) of Cr (III), Cu (II), and Zn (II) ions solutions with different weights of Attapulgite and Flint (0.005, 0.01, 0.05, 0.1, 0.3, 0.5 and 0.7) g and (0.2,0.3,0.4,0.5,0.6,0.7 and 0.8) g respectively at a specified temperature (298K), pH of Cr (III), Cu (II), and Zn (II) ions solutions were (3.8,3.4 and

7.3) respectively (actual pH of the aqueous solution without adjustment), shaking speed was (185)rpm and the contact time of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint were (30,40 and 90) minutes and (10,10 and 90) minutes respectively. After the equilibrium time elapsed, the two phases were separated by centrifuging (5000 rpm,5min.), then filtered by a filter paper. The metal ions concentration in aqueous state was measured by using an atomic absorption spectrophotometer.

3.6.3 Effect of pH

25 mL of fixed concentration (100 mg/L) of Cr (III), Cu (II), and Zn (II) ions solutions were agitated with (0.1,0.5 and 0.1) g of Attapulgite and (0.6,0.3 and 0.4) g of Flint respectively at temperature (298K), shaking speed was (185) rpm and the contact time of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint were (30,40 and90) minutes and (10,10, and 90) minutes respectively. pH of the solution was adjusted (1, 2, 3, 4, 5, and 7) by using HCL (0.1M) or NaOH (0.1M). After the equilibrium time, the two phases were separated by centrifuging (5000 rpm,5min.), then filtered by a filter paper. The metal cation concentration in aqueous state was measured by using an atomic absorption spectrophotometer.

3.6.4 Effect of temperature

25 mL of fixed concentration (100 mg/L) of Cr (III), Cu (II), and Zn (II) ions solutions were agitating with (0.1,0.5,and 0.1) g of Attapulgite and (0.6,0.3and 0.4g) of Flint respectively at pH = 3, shaking speed was (185)rpm and the contact time of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint were (30,40 and 90) minutes and (10,10 and 90) minutes respectively. Temperature of the solution was adjusted at (298, 308,

318 and 328)K. After the equilibrium time, the two phases were separated by centrifuging (5000 rpm,5min.), then filtered by a filter paper. The metal cation concentration in aqueous state was measured by using an atomic absorption spectrophotometer.

3.7 Adsorption isotherms study

To describe adsorption isotherms for Cr (III), Cu (II), and Zn (II) ions solutions on Attapulgite and Flint clay, the next procedures used were volumes of (25mL) of Cr (III), Cu (II), and Zn (II) ion solutions of identified concentrations (20, 60, 100, 140, 180 and 220) mg/L, were placed in volumetric flasks having (0.1, 0.5 and 0.1) g of Attapulgite and (0.6, 0.3 and 0.4) g of Flint respectively. At a specific temperature and with a pH = 3. For the required equilibrium time, the flasks were stirred by a thermostatically controlled stirrer at (185)rpm. After contact time ended, the two phases were separated by centrifuging (5000rpm, 5min.), then filtered by a filter paper. The metal cation concentration in aqueous phase was measured by using an atomic absorption spectrophotometer. The quantity of Cr (III), Cu (II), and Zn (II) ions adsorbed was measured from initial and final concentrations and volume of solution, according to the following equation[129].:

$$q_e = \frac{(C_\circ - C_e)V}{m_{Adsorbent}} \qquad \ldots 3.1$$

Whereas q_e represents adsorbed amount of adsorbate per weight of adsorbent (mg/g), C_e denotes solute concentration at equilibrium(mg/L), (V) denotes solution volume (L), and m denotes clays quantity (g).

The q_e of adsorption uptake is described as adsorbate amount in (mg) retained by (1g) of clay. Adsorption experiments were carried out at two different temperatures (298 and 318) K. The percentage removal of the adsorbate (%R) was computed using the formula follow [130].:

$$\%\boldsymbol{R} = \frac{(\boldsymbol{C}_{\circ} - \boldsymbol{C}_{e})}{\boldsymbol{C}_{\circ}} \times \mathbf{100} \qquad \ldots \mathbf{3.2}$$

3.8 Application of the optimum conditions

After adjusting all the optimum conditions (PH, adsorbent amount, contact time, and temperature) for adsorption of heavy metals Cr (III), Cu (II), and Zn (II) ions in mono-system onto Attapulgite and Flint clays from batch experiments onto synthetic water. The optimal conditions were applied on ternary heavy metals ions mixture and the Al-Quds power station wastewater samples.

Chapter Four

(Results and Discussion)

4.1 Atomic force microscopy (AFM)

Because of its excellent resolution abilities, atomic force microscopy (AFM) is an effective description device for surfaces at both the micro-and nanoscale **[131].** Figures (4.1 – 4.4) show AFM pictures for Attapulgite and Flint, respectively, with (size = 1538 X 1552 nm and size = 1528 X 1574 nm) and analytical capacity (pixel = 432,436 and 444, 456).

Figures (4.1 and 4.3) are three-dimensional (3D) AFM images that describe grain structure form, while Figures (4.2 and 4.4) are two-dimensional (2D) AFM images that reveal average roughness of (2.09 and 1.18) nm for Attapulgite and Flint respectively and the root mean square (RMS) are (2.41 and 1.38) nm for Attapulgite and Flint as well. The Attapulgite clay has a particle size of (90.0-180.0) nm, an average diameter (105.86) nm and a maximum height of (8.13) nm. While the Flint clay has a particle size of (30.0 - 68.0) nm, an average diameter (47.19)nm and maximum height of (4.793) nm. The granularity cumulating distribution and average diameter data of Attapulgite and Flint are shown in Tables (4.1 and 4.2), as well as Figures (4.5 and 4.6).

Although the morphology features of Flint clay was better than Attaplugite one according to AFM, the Attaplugite clay showed higher adsorption efficiency for heavy metals. This may be due to the chemical composition and crystalline structure of Attapulgite clays.

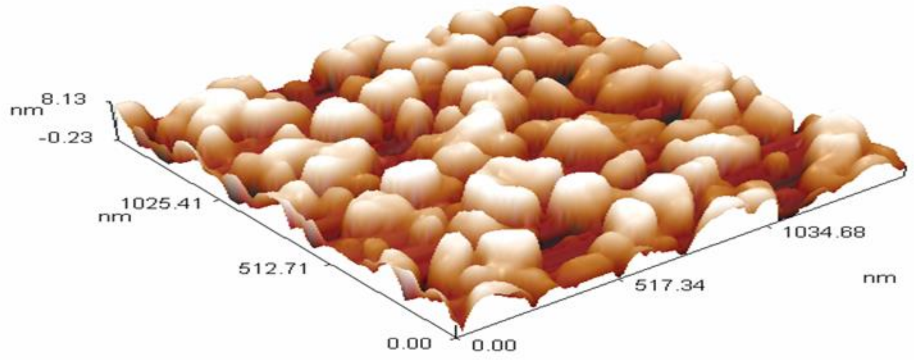


Fig. (4.1) AFM image(3D) for Attapulgite clay

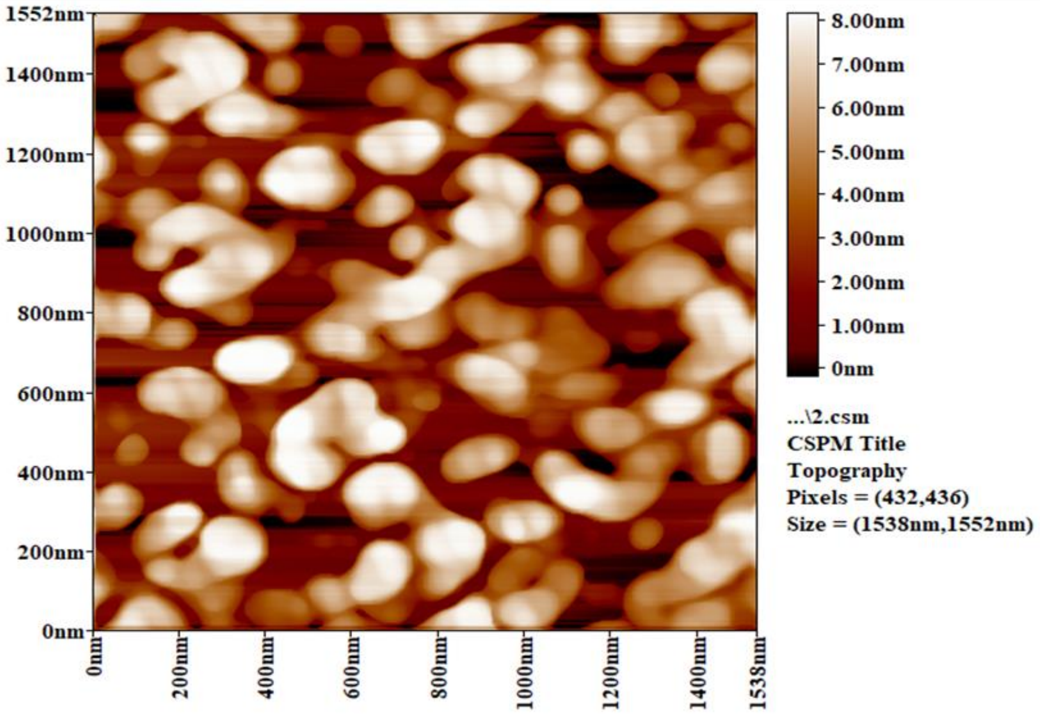


Fig. (4.2) AFM image(2D) for Attapulgite clay.

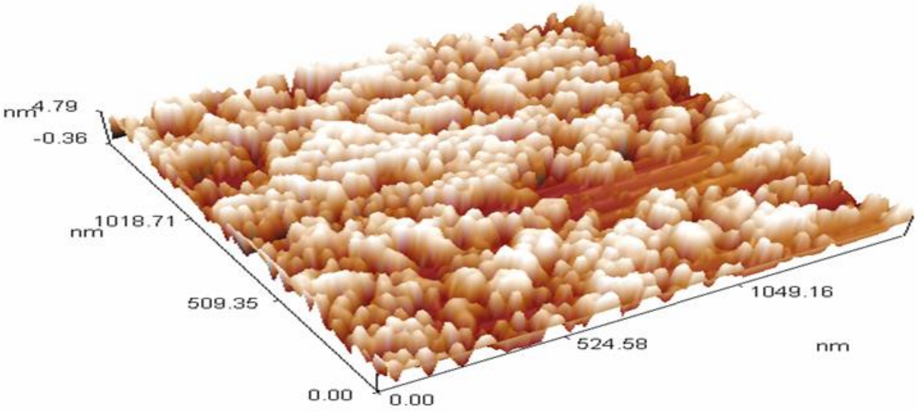


Fig. (4.3) AFM image(3D) for Flint clay.

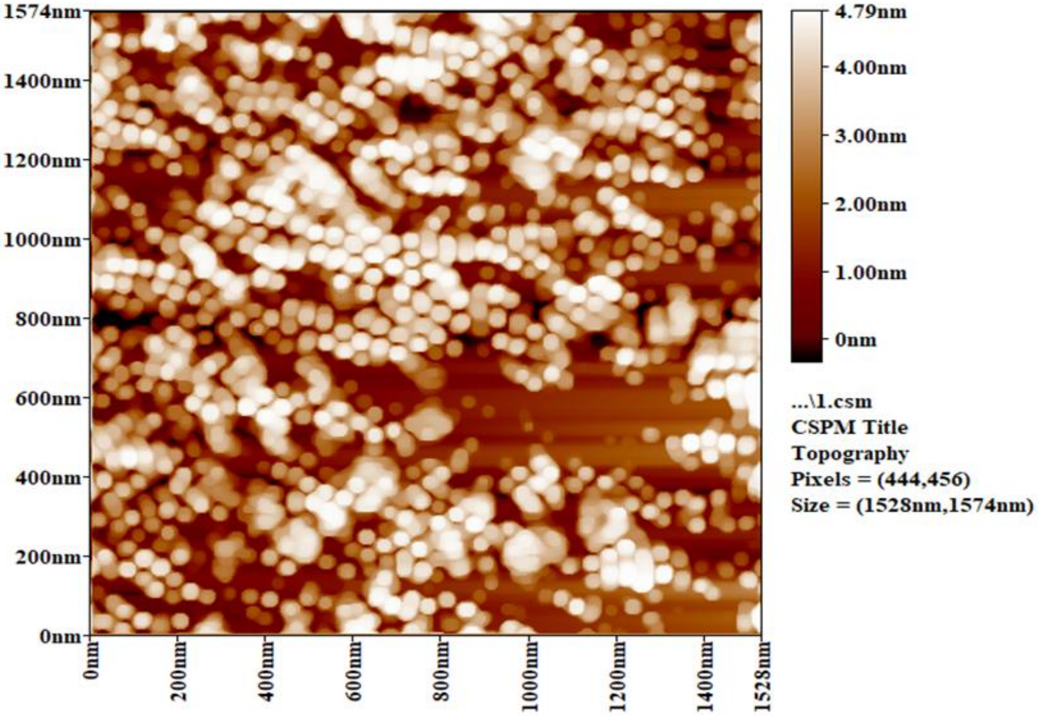


Fig. (4.4) AFM image(2D) for Flint clay.

Table (4.1) Granularity cumulating distribution and average diameter of Attapulgite clay.

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
90.00	32.05	32.05	130.00	3.85	83.33	170.00	2.56	98.72
100.00	19.23	51.28	140.00	5.13	88.46	180.00	1.28	100.00
110.00	16.67	67.95	150.00	6.41	94.87			
120.00	11.54	79.49	160.00	1.28	96.15			

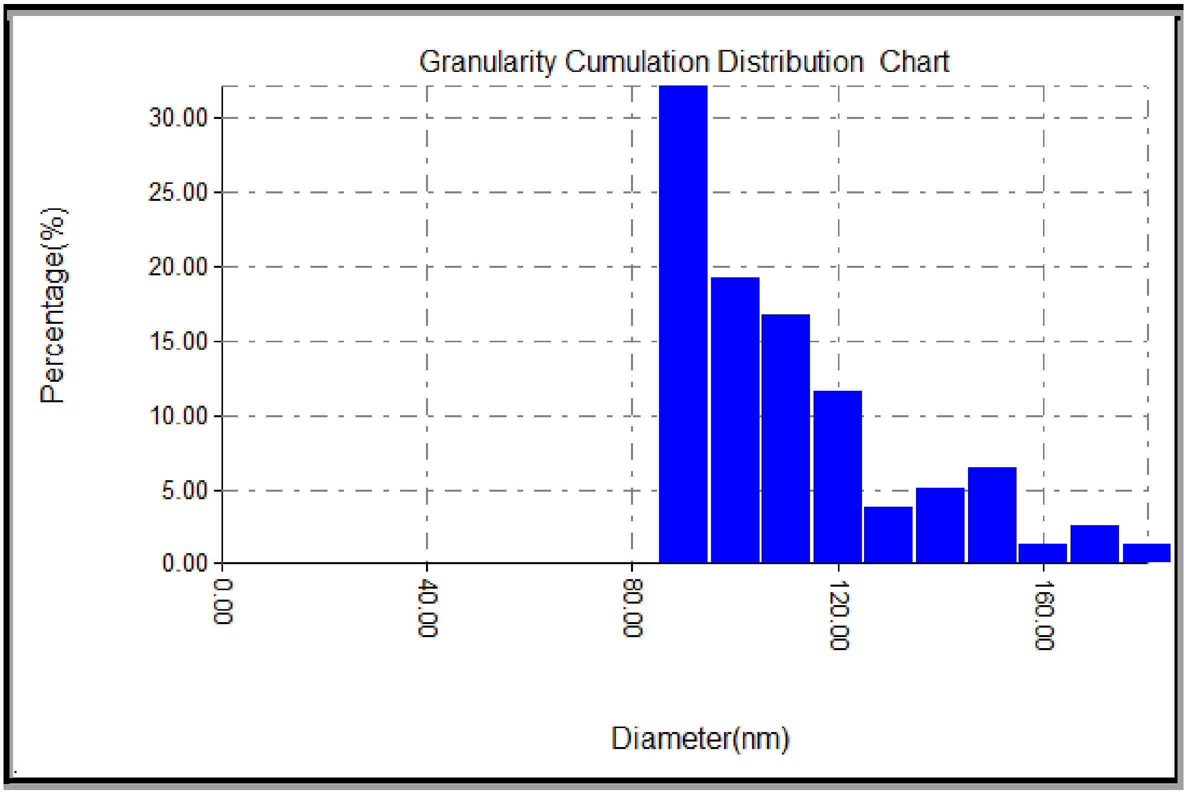


Fig. (4.5) Granularity cumulating distribution of Attapulgite.

Table (4.2) Granularity cumulating distribution and average diameter of Flint clay.

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
30.00	1.35	1.35	44.00	9.42	38.12	58.00	3.36	87.44
32.00	1.57	2.91	46.00	7.85	45.96	60.00	3.81	91.26
34.00	2.47	5.38	48.00	8.30	54.26	62.00	3.14	94.39
36.00	2.91	8.30	50.00	9.19	63.45	64.00	2.69	97.09
38.00	6.28	14.57	52.00	8.07	71.52	66.00	2.02	99.10
40.00	7.40	21.97	54.00	7.40	78.92	68.00	0.90	100.00
42.00	6.73	28.70	56.00	5.16	84.08			

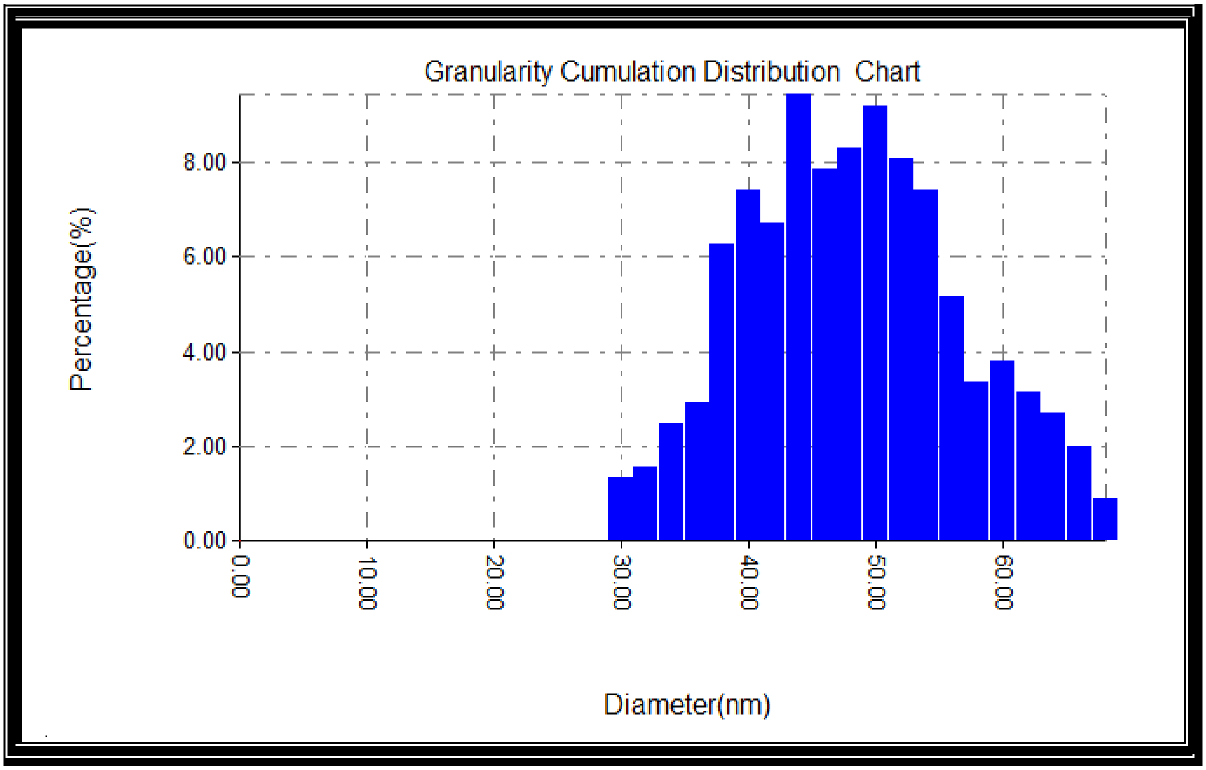


Fig. (4.6) Granularity cumulating distribution of Flint.

4.2 Study of factors affecting on adsorption process

4.2.1 Contact time effect

The effect of contact time on adsorption of Cr (III), Cu (II), and Zn (II) ions from their synthetic solutions in mono-system onto Attapulgite and Flint clays at 298K were studied using a fixed initial concentration (C_0 = 100 mg/L), pH = 3.8,3.4, and 7.3 respectively, fixed weight of the Attaplugite and Flint (0.05 and 0.3) g respectively, and tested at various periods (10 - 120) minute. The investigations were carried out in accordance with the procedures described in (section 3.6.1). Table (4.3) indicates the experimental data for the Attapulgite and Flint clays. The plots of q_t vs time are shown in Figures (4.7 and 4.8). The shortest time to achieve equilibrium for all systems are estimated using these curves, indicating that equilibration time requires between (10 – 90) minutes. The time required for Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint to attain equilibrium was (30,40, and 90) minutes and (10,10, and 90) minutes respectively. The results showed that adsorption capacities for Cr (III), Cu (II), and Zn (II) ions on Attapulgite clay and Zn (II) ions on Flint clay were rapidly increased for the first 10 minutes and continued gradually to increase to a certain time and then stabilized, whereas the adsorption capacities for Cr (III) and Cu (II) ions on Flint clay were increased for the first 10 minutes and then stabilized. The initial quick adsorption was most likely caused by initial concentration slope between amount of vacant sites available and adsorbate in solution on the Attapulgite and Flint surfaces. The steady increase in adsorption and, as a result, the achievement of equilibrium adsorption can be explained by the transfer of mass of adsorbate particles from bulk liquid to outer surfaces of Attapulgite and Flint clays [132] .

Table (4.3) Contact time effect on adsorption capacity and removal of Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clays at C_0 = 100 mg/L, $V_{solution}$ = 25 mL, particle size of 75 µm, and temperature = 298K.

clays		Metals ions								
		Cr (III)			**Cu (II)**			**Zn (II)**		
	Time(min.)	**C_e(mg/L)**	**%R**	**q_t(mg/g)**	**C_e(mg/L)**	**%R**	**q_t(mg/L)**	**C_e(mg/L)**	**%R**	**q_t(mg/g)**
Attapulgite	10	0.7860	99.2140	49.5670	9.4430	90.5569	45.2784	60.2336	39.7664	19.8832
	20	0.7860	99.2140	49.6070	9.2462	90.7537	45.3768	57.7742	42.2258	21.1129
	30	0.5300	99.4700	49.7350	8.9019	91.0980	45.5490	49.1663	50.8337	25.4168
	40	0.5200	99.4800	49.7400	8.5778	91.4221	45.7110	45.4772	54.5228	27.2614
	60	0.5000	99.5000	49.7500	8.5611	91.4388	45.7194	30.7208	69.2792	34.6396
	90	0.4570	99.5430	49.7715	8.5576	91.4424	45.7212	20.3145	79.6855	39.8427
	120	0.4570	99.5430	49.7715	8.5576	91.4424	45.7212	20.5642	79.4358	39.7179
Flint	10	69.2340	30.7660	2.5638	42.1715	57.8285	4.8190	68.8415	31.1585	2.5965
	20	69.3080	30.6920	2.5576	42.1623	57.8377	4.81980	62.6930	37.3070	3.1089
	30	69.3140	30.6860	2.5571	42.1508	57.8492	4.8207	57.7742	42.2258	3.5188
	40	70.2350	29.7650	2.4804	42.1506	57.8494	4.8207	56.5445	43.4555	3.6212
	60	71.0020	28.9980	2.4165	42.1504	57.8496	4.8208	47.9366	52.0634	4.3386
	90	69.0020	30.9980	2.5831	42.1462	57.8538	4.8211	43.0178	56.9822	4.7485
	120	69.0023	30.9977	2.5831	42.1462	57.8538	4.8211	43.9981	56.0019	4.6668

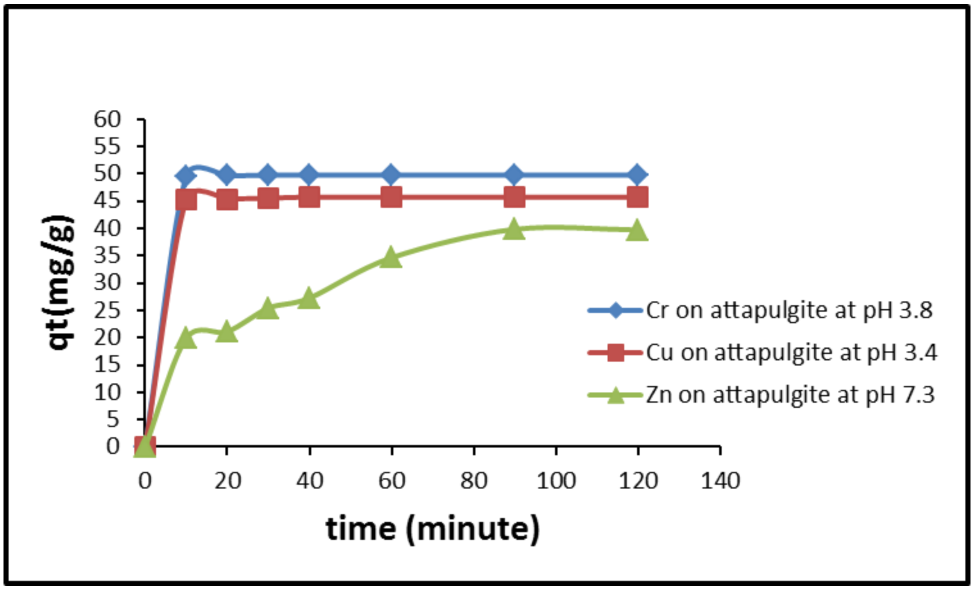


Fig. (4.7) Contact time effect on adsorption capacity of Cr (III), Cu (II), and Zn (II) ions on Attapulgite at C_0 = 100 mg/L, $V_{solution}$ = 25mL, pH = 3.8,3.4, and 7.3 respectively, Attapulgite dose = 0.05 g, and temperature = 298K.

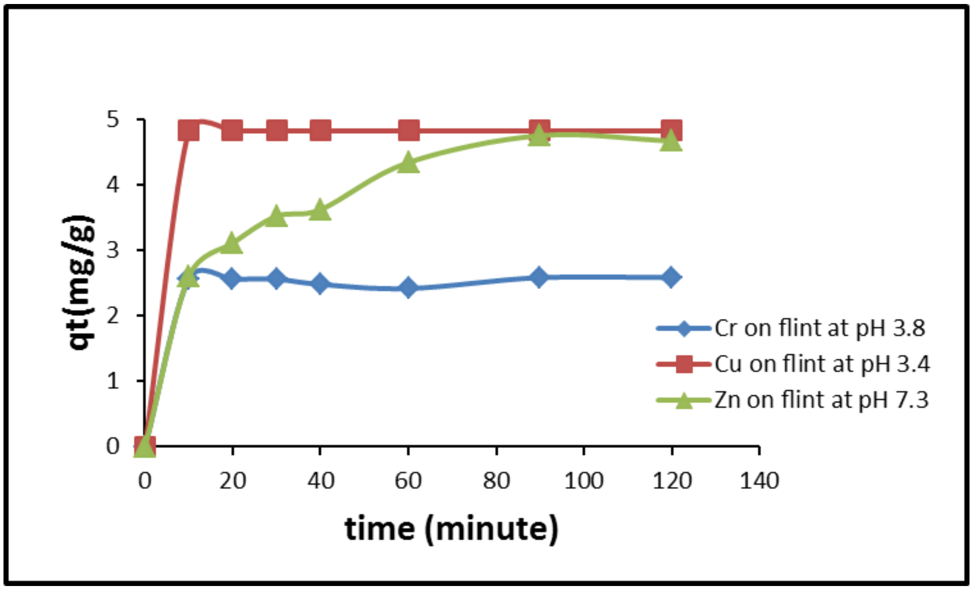


Fig. (4.8) Contact time effect on adsorption capacity of Cr (III), Cu (II), and Zn (II) ions on Flint at C_0 = 100 mg/L, $V_{solution}$ = 25mL, pH = 3.8,3.4, and 7.3 respectively, Flint dose 0.3 g, and temperature = 298K.

4.2.2 Dosage effect

Adsorbent dosage is an essential factor for it specifies the adsorption capacity for a known primary concentration of the adsorbate molecules at the operating conditions. The effect of Attapulgite and Flint clay doses for adsorption of the Cr (III), Cu (II), and Zn (II) ions from their synthetic solutions in mono-system at 298K were studied by using a fixed initial concentration (C_0 = 100 mg/L), pH = 3.8,3.4, and 7.3 respectively, contact time on Attapulgite = (30,40, and 90) min.and contact time on Flint = (10,10,and 90) min. respectively, and tested at various doses of clays. The investigations were carried out in accordance with the procedures described in (section 3.6.2). The effects of doses reselts of Attapulgite and Flint clays on Cr (III), Cu (II), and Zn (II) ions adsorption are shown in Table (4.4) and Figures (4.9 (a-c) and 4.10 (a-c)). The experimental results indicate that when the quantity of adsorbents were increased, the adsorption capacity decreased till the perfect dose were achieved, after which it stayed unchanged regardless of the quantity of adsorbents. As expected, equilibrium concentration decreases with increasing adsorbent quantities for a known initial Cr (III), Cu (II), and Zn (II) ions concentration.

Perhaps this is due to fast increase in surface area and the occurrence of as many adsorption active positions than when adsorbent quantity was increased [133,134]. As the weight of the adsorbents increases, the curves nears a plateau, as seen in Figures (4.7 (a-c) and 4.8(a-c)). This plateau value denotes adsorption processes equilibrium stage. Attapulgite has plateau values for adsorption of Cr (III), Cu (II), and Zn (II) ions of (0.1,0.5 and 0.1) g respectively. Flint has plateau values for adsorption of Cr (III), Cu (II), and Zn (II) ions of (0.6,0.3, and 0.4) g, respectively.

Table (4.4) Dosage effect on adsorption capacity and removal of Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clays at C_0 = 100 mg/L, $V_{solution}$ = 25 mL, particle size of 75 µm, and temperature = 298K.

Clays		**Metals ions**								
		Cr (III)			**Cu (II)**			**Zn (II)**		
	Dosage(g)	**Ce(mg/L)**	**%R**	**q_e(mg/g)**	**Ce(mg/L)**	**%R**	**q_e(mg/L)**	**Ce(mg/L)**	**%R**	**q_e(mg/g)**
Attapulgite	0.005	8.3657	91.6300	458.1700	6.9750	93.0300	465.1300	41.1841	58.8200	294.0800
	0.01	5.8750	94.1300	235.3100	6.7240	93.2800	233.1900	39.9544	60.0500	150.1100
	0.05	2.7600	97.2400	48.6200	5.8090	94.1900	47.1000	39.8395	60.1600	30.0800
	0.1	0.0520	98.9500	24.9900	5.4650	94.5400	23.6300	38.1098	61.8900	15.4700
	0.3	0.0510	99.9500	8.3300	2.5280	97.4700	8.1200	38.8801	61.1200	5.0900
	0.5	0.0500	99.9500	5.0000	0.6440	99.3600	4.9700	38.4066	61.5900	3.0800
	0.7	0.0530	99.9500	3.5700	0.6440	99.3600	3.5500	37.9425	62.0600	2.2200
	0.9	0.0500	99.9500	2.7800	0.6430	99.3600	2.7600	37.6542	62.3500	1.7300
Flint	0.2	73.6820	26.3200	3.2900	40.5895	59.4100	7.4300	40.5692	59.4300	7.4300
	0.3	68.1939	31.8100	2.6500	39.8984	60.1000	5.0100	38.7247	61.2800	5.1100
	0.4	61.5093	38.4900	2.4100	39.8984	60.1000	3.7600	30.1168	69.8800	4.3700
	0.5	53.7656	46.2300	2.3100	39.8293	60.1700	3.0100	30.8871	69.1100	3.4600
	0.6	45.6578	54.3400	2.2600	39.6220	60.3800	2.5200	30.4277	69.5700	2.9000
	0.7	45.7542	54.2500	1.9400	39.6331	60.3700	2.1600	30.2792	69.7200	2.4900
	0.8	45.9981	54.0000	1.6900	39.6423	60.3600	1.8900	30.2658	69.7300	2.1800

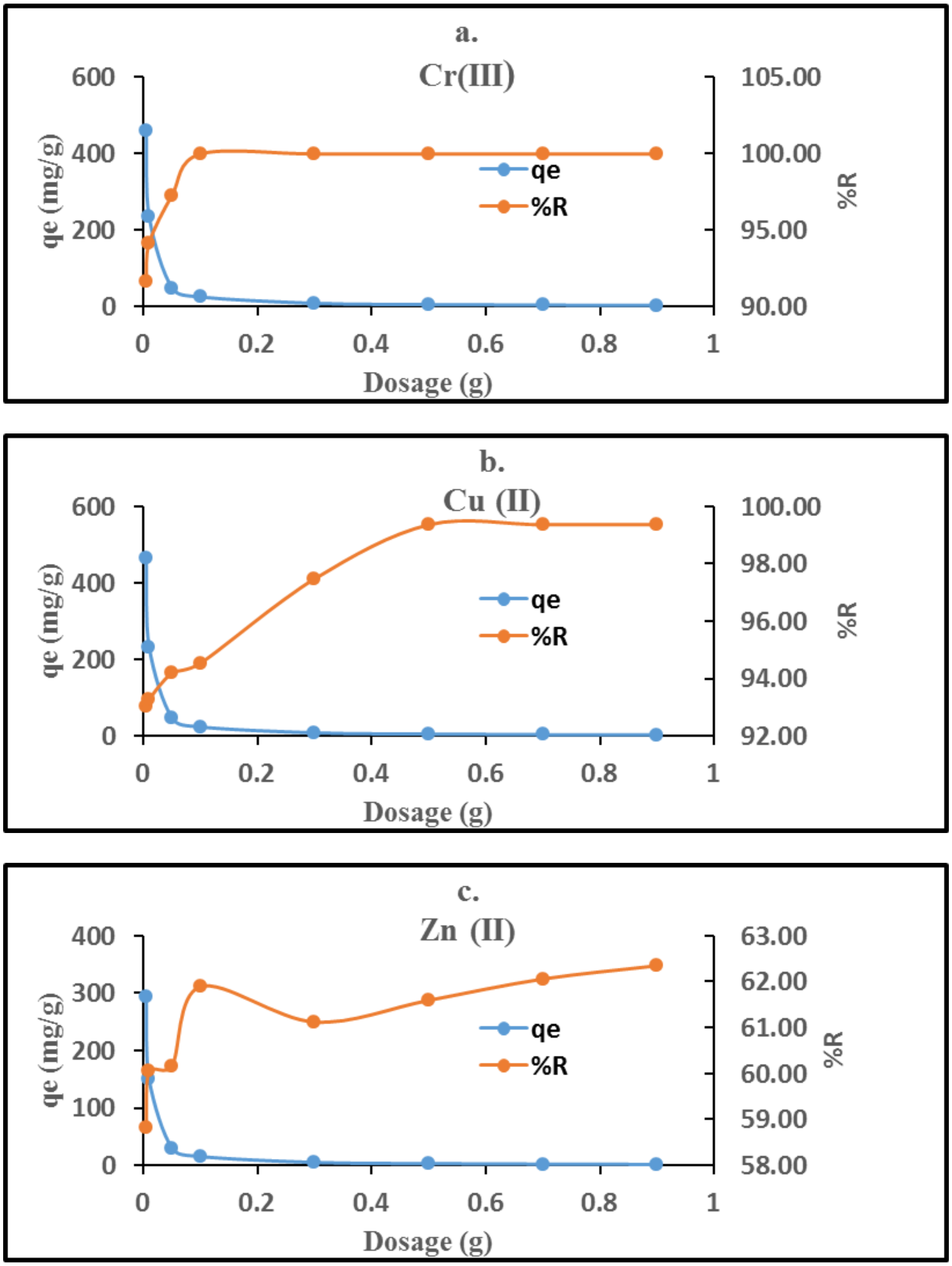


Fig. (4.9a-c) Attapulgite dosage effect on adsorption capacity and removal of Cr (III), Cu (II), and Zn (II) ions at C_0 = 100 mg/L, $V_{solution}$ =25 mL, pH = (3.8,3.4, and 7.3), contact time = (30,40, and 90) minutes respectively, and temperature = 298K.

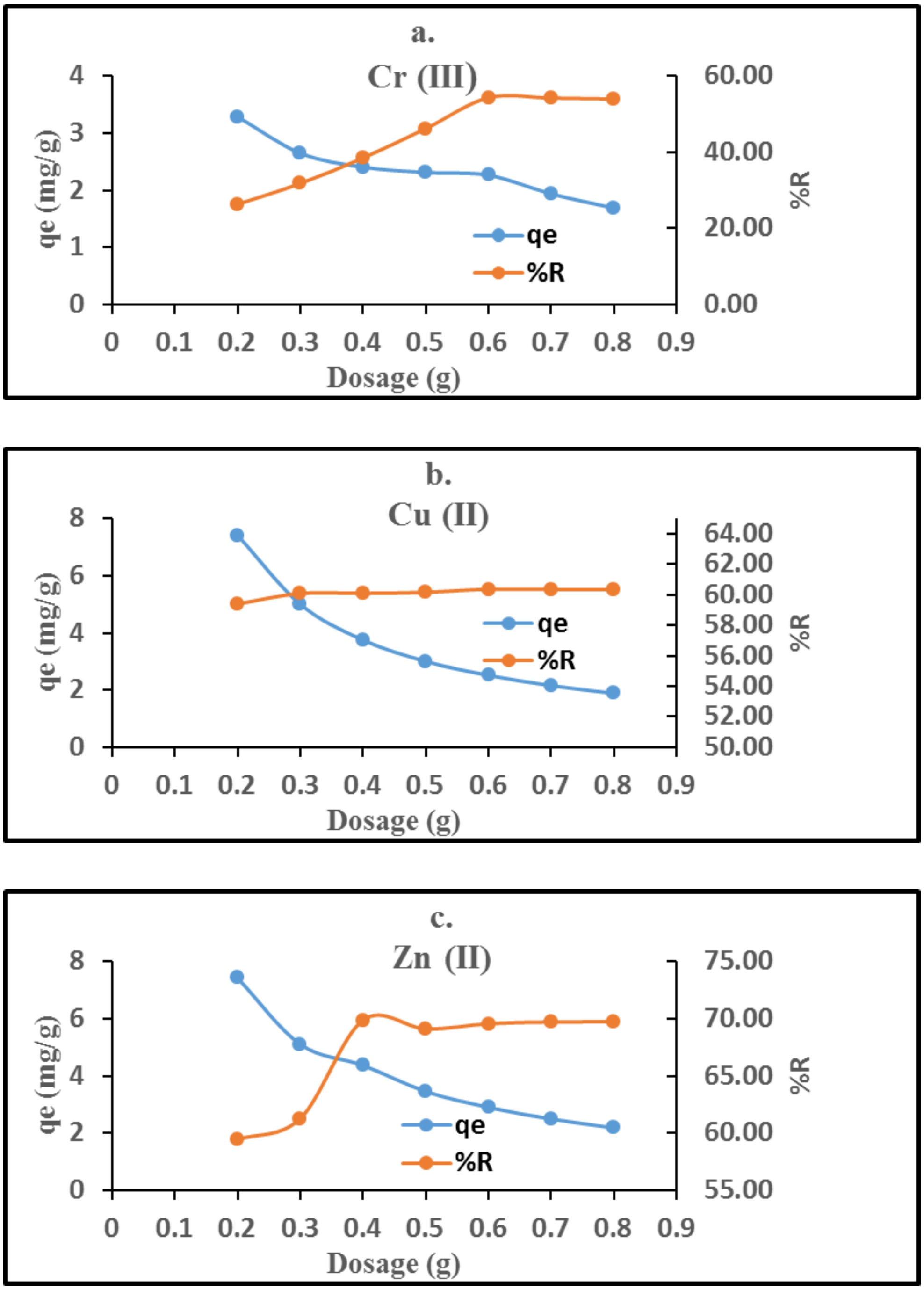


Fig. (4.10a-c) Flint dosage effect on adsorption capacity and removal of Cr (III), Cu (II), and Zn (II) ions at C_0 = 100 mg/L, $V_{solution}$ =25 mL pH = (3.8,3.4, and 7.3), contact time = (10,10, and 90) minutes respectively, and temperature = 298K.

4.2.3 pH effect

Among the most important factors in studying an adsorbent's adsorption property is the pH of the aqueous solution[135]. pH effect for adsorption of the Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clays from their synthetic solutions in monosystem at 298K were studied by using a fixed initial concentration (C_o=100 mg/L), $V_{solution}$=25mL, contact time on attapulgite = 30,40, and 90 min., and contact time on Flint = 10,10, and 90 min. respectively, and tested at different pH (1-7). The investigations were carried out in accordance with the procedures described in (section 3.6.3). pH effect on adsorption of Cr (III),Cu (II), and Zn (II) ions are shown in Table (4.5) and figures (4.11 and 4.12). The experimental data exhibited that the adsorption of Cr (III),Cu (II), and Zn (II) ions onto Attapulgite and Flint were greatly reliant on pH, which affects the ionization extent,surface charges, and adsorbent type [136]. The adsorption of Cr (III) and Cu (II) ions onto Attapulgite and Flint was low under highly acidic conditions, but rapidly bettered as the solution pH increased between (1-5). This could be due to competition for adsorption on ions exchange positions in the acid range (1-3) between Cr (III) and Cu (II) ions and H^{+1} ions, leading to low removal of Cr (III) and Cu (II) ions [137,138]. On the other hand, the adsorption of Zn (II) ions onto Attapulgite and Flint increased as the pH of the solution increased between (1-4) and then decreased at pH = 5. The increase in pH range (1-4) may be results from decreased competation between Zn(II) ions and (H^{+1}) ions, while decrease in pH = 5 results from increased competation between Zn (II) ions and (OH^{-1}) ions [139]. Many experiments were halted due to the precipitation of Cr (III) and Cu (II) ions in the solution at pH levels greater than (5) and precipitation of Zn (II) ions at pH (9 and 11)[137].

Table (4.5) pH effect on adsorption capacity and removal of Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clays at C_0 = 100 mg/L, $V_{solution}$ = 25 mL , particle size of 75 µm,and temperature = 298K.

Clays		**Metals ions**								
		Cr (III)			**Cu (II)**			**Zn (II)**		
	pH.	**Ce(mg/L)**	**%R**	**q_e(mg/g)**	**Ce(mg/L)**	**%R**	**q_e(mg/L)**	**Ce(mg/L)**	**%R**	**q_e(mg/g)**
Attapulgite	**1**	**76.1481**	**23.8518**	**5.9629**	**29.6356**	**70.3644**	**3.5182**	**34.6541**	**65.3459**	**16.3364**
	2	**15.2112**	**84.7887**	**21.1971**	**14.5674**	**85.4326**	**4.2716**	**27.2743**	**72.7256**	**18.1814**
	3	**6.5621**	**93.4379**	**23.3594**	**10.6780**	**89.3220**	**4.4661**	**25.1987**	**74.8012**	**18.7003**
	4	**0.0000**	**100.0000**	**25.0000**	**2.4567**	**97.5433**	**4.8771**	**24.5689**	**75.4310**	**18.8577**
	5	**0.0000**	**100.0000**	**25.0000**	**0.0550**	**99.945**	**4.9972**	**30.9641**	**69.0359**	**17.2589**
	7	**-**	**-**	**-**	**-**	**-**	**-**	**36.3467**	**63.6533**	**15.9133**
Flint	**1**	**76.7225**	**23.2774**	**0.9698**	**56.7800**	**43.2200**	**3.6016**	**33.2746**	**66.7254**	**4.1703**
	2	**71.9555**	**28.0445**	**1.1685**	**48.2607**	**51.7393**	**4.3116**	**27.9629**	**72.0370**	**4.5023**
	3	**67.0644**	**32.9356**	**1.3723**	**45.7800**	**54.2200**	**4.5183**	**26.1987**	**73.8012**	**4.6125**
	4	**51.0799**	**48.9200**	**2.0383**	**37.6860**	**62.3140**	**5.1928**	**25.2576**	**74.7424**	**4.6714**
	5	**45.8658**	**54.1341**	**2.2555**	**35.6780**	**64.3220**	**5.3601**	**29.6983**	**70.3017**	**4.3938**
	7	**-**	**-**	**-**	**-**	**-**	**-**	**31.5896**	**68.4104**	**4.2756**

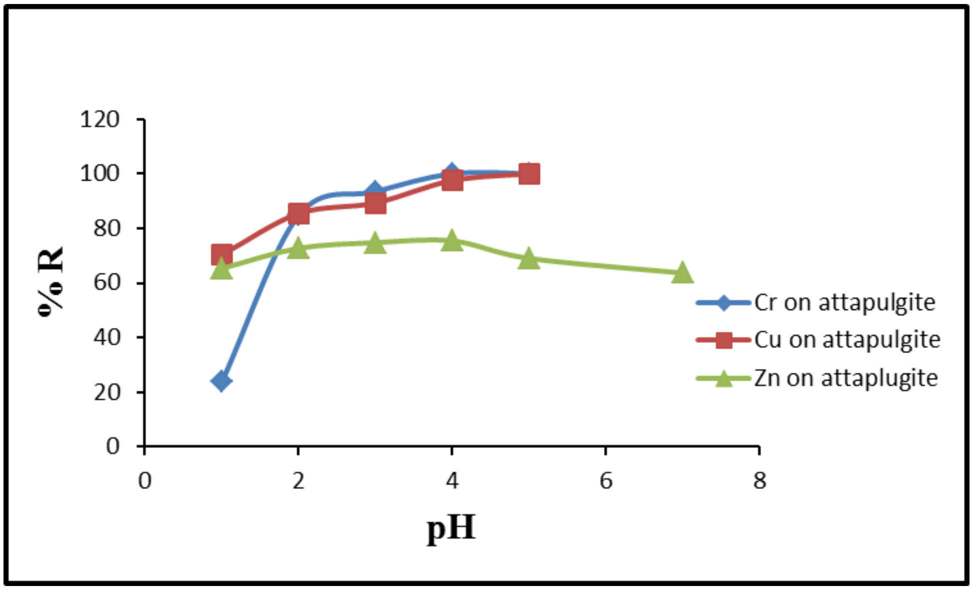


Fig.(4.11) pH effect on removal of Cr (III), Cu (II), and Zn (II) ions on Attapulgite at C_0 = 100 mg/L, $V_{solution}$ = 25 mL ,Attapulgite dose = (0.1,0.5 and 0.1) g, contact time = (30,40, and 90) minutes respectively and temperature = 298K.

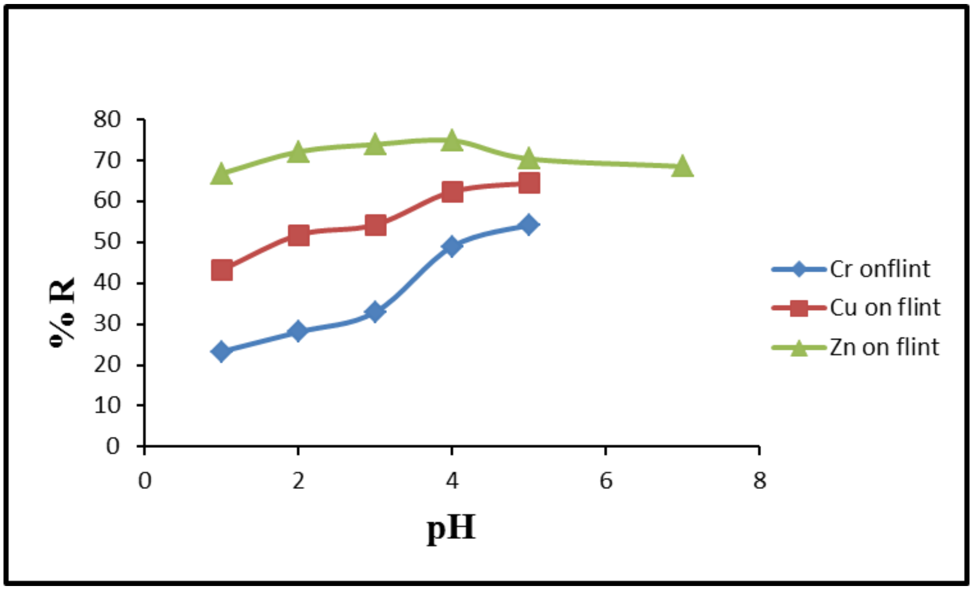


Fig.(4.12) pH effect on removal of Cr (III), Cu (II), and Zn (II) ions on Flint at C_0 = 100 mg/L, $V_{solution}$ = 25 mL, Flint dose (0.6,0.3 and 0.4) g,contact time = (10,10,and 90) minutes respectively and temperature = 298K.

4.2.4 Temperature effect

Temperature effect on adsorption of Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clays from their synthetic solutions in mono-system at pH = 3 were studied using a fixed initial concentration (C_o = 100 mg/L), $V_{solution}$ = 25 mL, contact time on Attapulgite = (30,40, and 90) minutes, and contact time on Flint = (10,10, and 90) minutes, Attapulgite dose = (0.1,0.5 and 0.1) g, Flint dose =(0.6,0.3 and 0.4) g respectively, and tested at different temperature (298,308,318,and 328)K. The investigations were carried out in accordance with the procedures described in (section 3.6.4).

Temperature effect on adsorption of Cr (III), Cu (II), and Zn (II) ions is seen in Table (4.6) and Figures (4.13 and 4.14). The experimental data showed that adsorption of Cr (III), Cu (II), and Zn (II) ions onto the Attapulgite and Cr (III) and Zn (II) ions onto Flint increase with increase in temperature (adsorption is endothermic process). This could be because as the temperature increases, more ions diffuse inside the crystal lattice of the clay **[140]**. In contrast, the adsorption capacity of copper (II) on Flint clay decreases with increasing temperature (adsorption is an exothermic process), this could be due to a weakening reaction force between copper ions and adsorption surface active sites as temperature increases **[141]** .

Table (4.6) Temperature effect on adsorption capacity and removal of Cr (III), Cu (II), and Zn (II) ions onto Attapulgite and Flint clays at C_0 = 100 mg/L,pH = 3, $V_{solution}$ = 25 mL ,and particle size of 75 µm.

Clays		**Metals ions**								
		Cr (III)			**Cu (II)**			**Zn (II)**		
	Temp.(K)	**C_e(mg/L)**	**%R**	**q_e(mg/g)**	**C_e(mg/L)**	**%R**	**q_e(mg/g)**	**C_e(mg/L)**	**%R**	**q_e(mg/g)**
Attapulgite	298	4.6380	95.3620	23.8405	15.5432	84.4568	4.2228	43.5621	56.4379	14.1094
	308	2.7626	97.2373	24.3093	9.6245	90.3755	4.5187	33.7462	66.2538	16.5634
	318	0.0000	100.0000	25.0000	2.6751	97.3249	4.8662	24.6834	75.3166	18.8291
	328	0.0000	100.0000	25.0000	0.0000	100.0000	5.0000	19.6421	80.3579	20.0894
Flint	298	52.7451	47.2549	1.9689	54.7860	45.2140	3.7678	47.3156	52.6844	3.2927
	308	48.6231	51.3769	2.1407	59.6753	40.3247	3.3603	42.6139	57.3861	3.5866
	318	44.3124	55.6876	2.3203	68.6742	31.3258	2.6104	35.4912	64.5088	4.0318
	328	42.4567	57.5433	2.3976	74.1256	25.8744	2.1562	29.7821	70.2179	4.3886

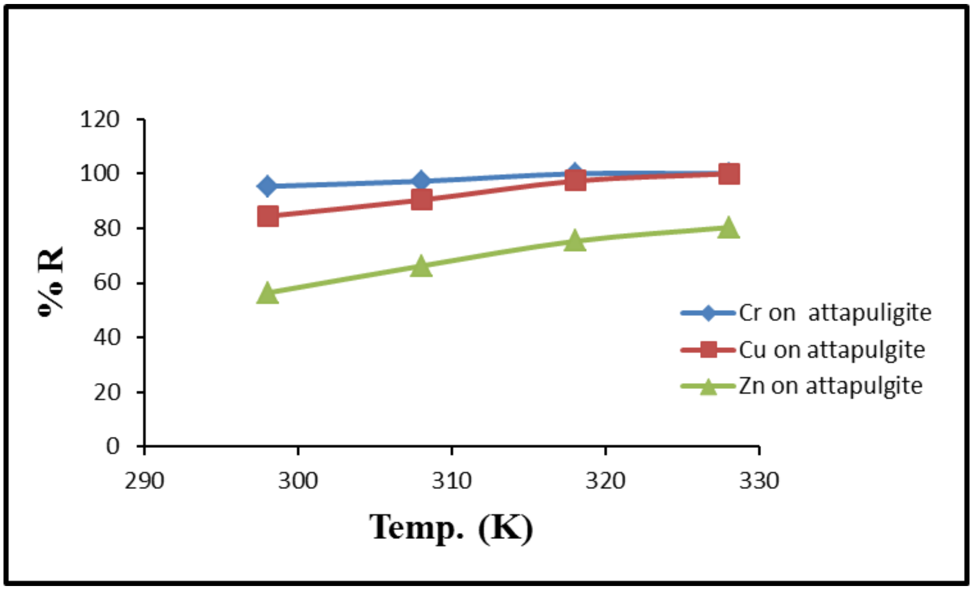


Fig.(4.13) Temperature effect on removal of Cr (III), Cu (II), and Zn (II) ions on Attapulgite at C_0 = 100 mg/L, pH = 3, $V_{solution}$ = 25 mL ,Attapulgite dose = (0.1,0.5,and 0.1) g and contact time = (30,40,and 90) minutes respectively.

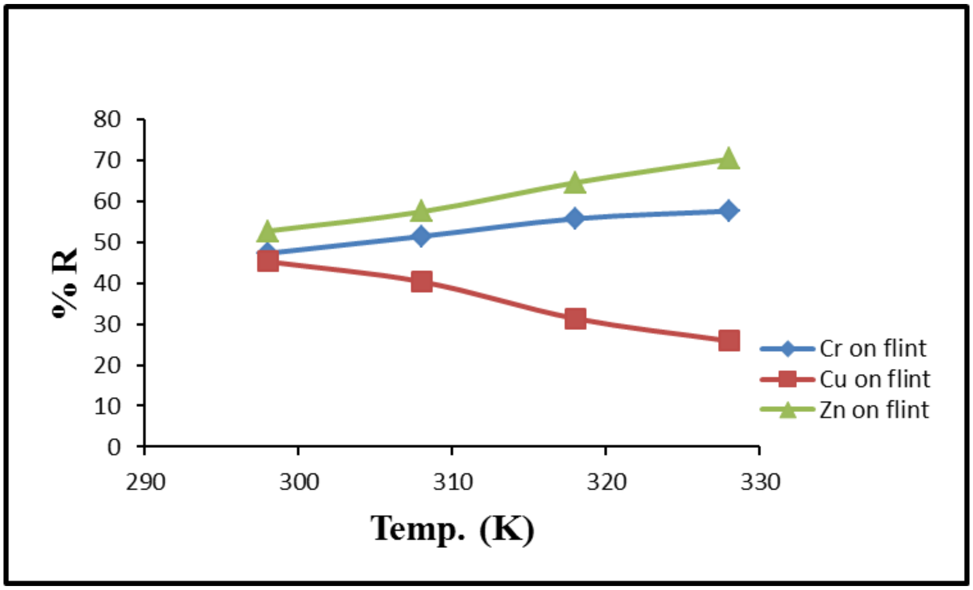


Fig.(4.14) Temperature effect on removal of Cr (III), Cu (II), and Zn (II) ions on Flint at C_0 = 100 mg/L, pH = 3, $V_{solution}$ = 25 mL, Flint dose = (0.1,0.5,and 0.1) g, and contact time = (10,10,and 90) minutes respectively.

4.3 Kinetic study

The mechanism of sorption and potential rate-governing procedures have been studied using kinetic models, which will aid in the choosing the optimal operating conditions for full-range batch system. Furthermore, sorption kinetics is important in wastewater treatment because it offers important insights into mechanism of sorption reaction and reaction pathways [142].Pseudo-first-order,pseudo-second-order, and intraparticle diffusion kinetic models were used in this study.

4.3.1 Pseudo first order model

In general, the pseudo-first-order rate depending on solid capacity is described as follow [143] :

$$\frac{d_{q_t}}{d_t} = k_1(q_e - q_t) \qquad \ldots 4.1$$

Which can be integrated into the following:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \ldots 4.2$$

Where k_1 represents pseudo-first-order rate constant (min^{-1}) q_e (mg/g) represents quantity of Cr (III), Cu (II), and Zn (II) ions adsorbed at equilibrium and q_t (mg/g) denotes quantity of Cr (III), Cu (II), and Zn (II) ions adsorbed at time (t).Table (4.7) shown a calculations. Table (4.10) and Figure (4.15 a-c) shown first order kinetic data from which k_1 from slope of plot of $\ln(q_e\text{-}q_t)$ vs (t). The pseudo-first-order model for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint were studied at C_0 = 100 mg/L, pH = 3, $V_{solution}$ = 25 mL Attapulgite dose = (0.1,0.5, and 0.1) g, Flint dose= (0.6,0.3, and 0.4) g respectively, and temperature = 298K.

Table (4.7) The calculations of Cr (III), Cu (II),and Zn (II) ions adsorption onto Attapulgite and Flint clay using pseudo-first-order model after applying experimental data.

clays		Metals ions								
		Cr (III)			Cu (II)			Zn (II)		
	Time (min.)	C_e (mg/L)	q_t (mg/g)	$\ln(q_e-q_t)$	C_e (mg/L)	q_t (mg/g)	$\ln(q_e-q_t)$	C_e (mg/L)	q_t (mg/g)	ln(qe-qt)
Attapulgite	**10**	**2.6540**	**24.3365**	**-1.2549**	**3.4445**	**4.8277**	**-2.5886**	**68.8523**	**7.7869**	**1.8012**
	20	**2.5640**	**24.3590**	**-1.3371**	**2.3257**	**4.8837**	**-3.9538**	**63.3187**	**9.1703**	**1.5419**
	30	**1.8342**	**24.5414**	**-2.5238**	**1.9654**	**4.9017**	**-6.7550**	**60.8593**	**9.7851**	**1.4008**
	40	**1.8356**	**24.5411**	**-2.5194**	**1.9543**	**4.9022**	**-7.4004**	**49.1771**	**12.7057**	**0.1293**
	60	**1.9286**	**24.5178**	**-2.2657**	**2.0000**	**4.9023**	**-7.4965**	**44.8138**	**13.7965**	**-3.0516**
	90	**1.7136**	**24.5715**	**-2.9956**	**1.9535**	**4.9023**	**-7.4698**	**44.7247**	**13.8188**	**-3.6886**
	120	**1.5136**	**24.6216**	**-**	**1.9421**	**4.9028**	**-**	**44.6247**	**13.8438**	**-**
Flint	**10**	**51.5340**	**2.0194**	**-2.9218**	**47.7520**	**4.3539**	**-2.9725**	**65.1632**	**2.1772**	**-0.0754**
	20	**51.4080**	**2.0246**	**-3.0244**	**47.3421**	**4.3881**	**-4.0760**	**59.0147**	**2.5615**	**-0.6105**
	30	**51.4140**	**2.0244**	**-3.0193**	**47.3532**	**4.3872**	**-4.0229**	**57.7850**	**2.6384**	**-0.7631**
	40	**51.3350**	**2.0277**	**-3.0891**	**47.3543**	**4.3871**	**-4.0178**	**55.3256**	**2.7921**	**-1.1631**
	60	**50.6450**	**2.0564**	**-4.0868**	**47.4267**	**4.3811**	**-3.7286**	**54.0959**	**2.8690**	**-1.4454**
	90	**50.8470**	**2.0480**	**-3.6805**	**47.2954**	**4.3920**	**-4.3364**	**50.4068**	**3.0995**	**-5.2841**
	120	**50.2420**	**2.0732**	**-**	**47.1384**	**4.4051**	**-**	**50.3257**	**3.1046**	**-**

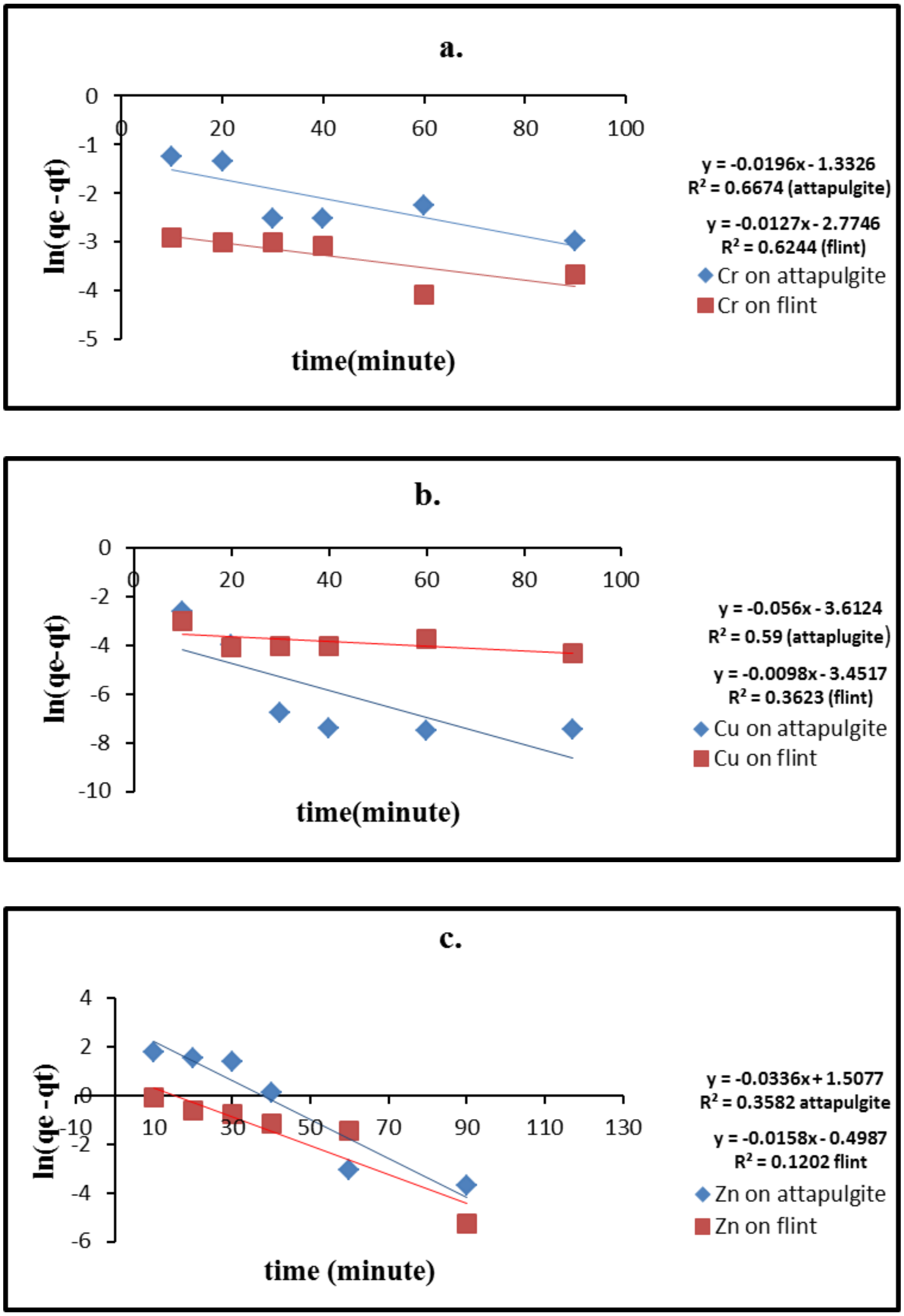


Fig.(4.15 a-c) Pseudo-first-order model of Cr (III), Cu (II), and Zn (II) ions adsorption on Attapulgite and Flint at C_0 = 100 mg/L, pH = 3, $V_{solution}$ = 25mL, and temperature = 298K.

4.3.2 Pseudo second order model

In general, the pseudo-second-order rate depending on solid capacity is described as follows [144] :

$$\frac{d_{q_t}}{d_t} = k_2(q_e - q_t)^2 \qquad \ldots 4.3$$

Which can be integrated into the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad \ldots 4.4$$

Whereas K_2 denotes the pseudo-second-order rate constant (g/mg.min.). The slopes and intercepts of linear plot of (t/q_t) vs (t), Figure (4.16), have been used to determine the values of K_2 and q_e, which are seen in Table (4.10). Table (4.8) shown a calculations. The pseudo-second-order model for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint were studied at C_0=100 mg/L, pH = 3, $V_{solution}$ = 25 mL Attapulgite dose = (0.1,0.5, and 0.1) g, Flint dose= (0.6,0.3, and 0.4) g respectively, and temperature = 298K.

Table (4.8) The calculations of Cr (III), Cu (II),and Zn (II) ions adsorption onto Attapulgite and Flint clay using pseudo second-order model after applying experimental data.

clays		Metals ions								
		Cr (III)			Cu (II)			Zn (II)		
	Time (min.)	C_e (mg/L)	q_t (mg/g)	t/q_t (min.g/mg)	C_e (mg/L	q_t (mg/g)	t/q_t (min.g/mg)	C_e (mg/L)	q_t (mg/g)	t/q_t (min.g/mg)
Attapulgite	10	2.6540	24.3365	0.4109	3.4445	4.8277	2.0713	68.8523	7.7869	1.2842
	20	2.5640	24.3590	0.8210	2.3257	4.8837	4.0952	63.3187	9.1703	2.1809
	30	1.8342	24.5414	1.2224	1.9654	4.9017	6.1202	60.8593	9.7851	3.0658
	40	1.8356	24.5411	1.6299	1.9543	4.9022	8.1594	49.1771	12.7057	3.1481
	60	1.9286	24.5178	2.4471	2.0000	4.9023	12.2390	44.8138	13.7965	4.3489
	90	1.7136	24.5715	3.6627	1.9535	4.9023	18.3586	44.7247	13.8188	6.5128
	120	1.5136	24.6216	4.8737	1.9421	4.9028	24.4753	44.6247	13.8438	8.6681
Flint	10	51.5340	2.0194	4.9519	47.752	4.3539	2.2967	65.1632	2.1772	4.5928
	20	51.4080	2.0246	9.8781	47.3421	4.3881	4.5577	59.0147	2.5615	7.8076
	30	51.4140	2.0244	14.8190	47.3532	4.3872	6.8380	57.7850	2.6384	11.3703
	40	51.3350	2.0277	19.7267	47.3543	4.3871	9.1175	55.3256	2.7921	14.3258
	60	50.6450	2.0564	29.1763	47.4267	4.3811	13.6951	54.0959	2.8690	20.9131
	90	50.8470	2.0480	43.9444	47.2954	4.3920	20.4915	50.4068	3.0995	29.0362
	120	50.2420	2.0732	57.8801	47.1384	4.4051	27.2409	50.3257	3.1046	38.6517

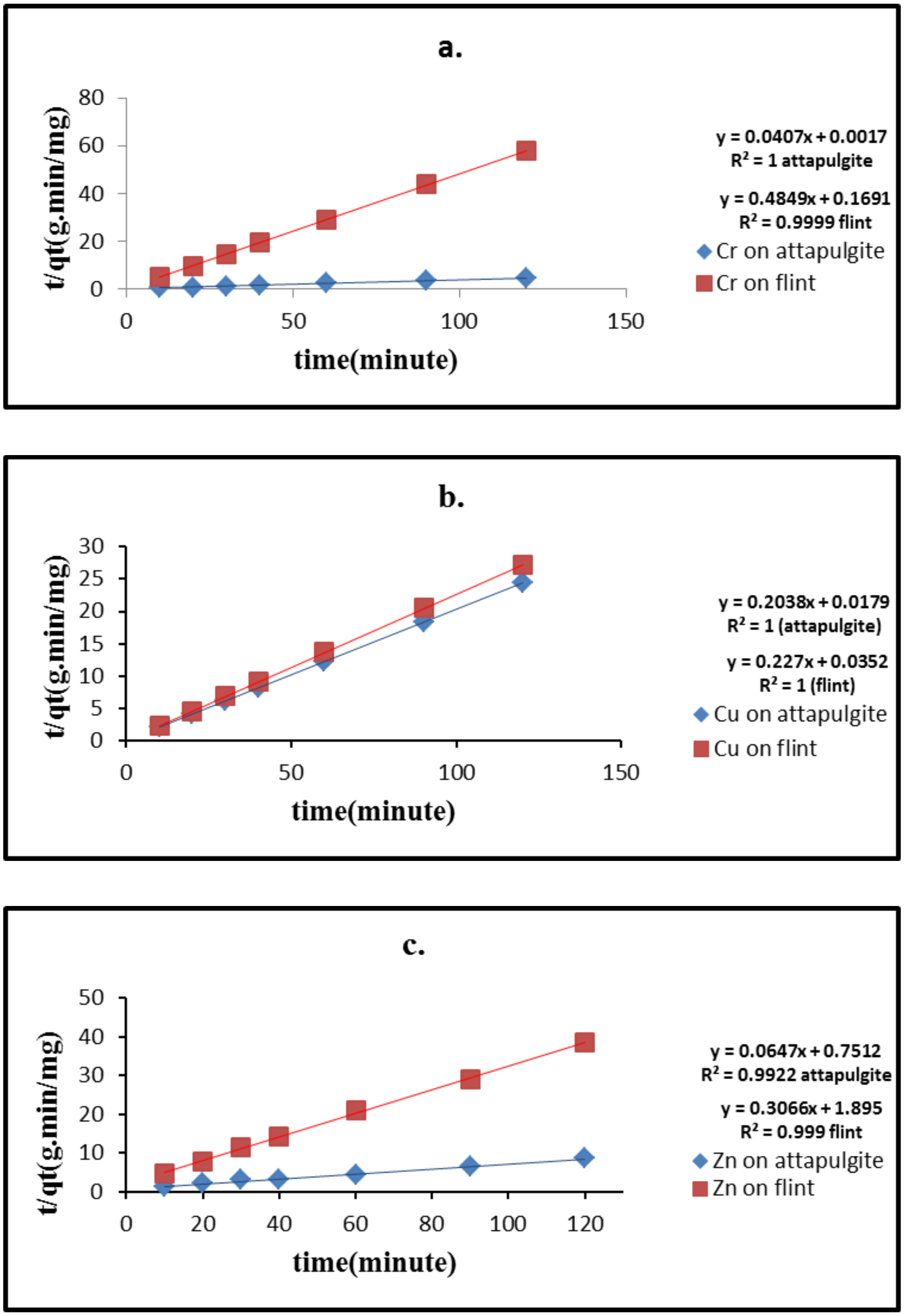


Fig.(4.16 a-c) Pseudo-second-order model of Cr (III), Cu (II), and Zn (II) ions adsorption on Attapulgite and Flint at C_0 = 100 mg/L, pH = 3, $V_{solution}$ = 25 mL, and temperature = 298K.

4.3.3 Intra-particle diffusion model

Although the pseuo-first-order and pseudo-second-order kinetic models are unable to classify the diffusion mechanism, the kinetic results possibly used to assess intraparticle diffusion occurrence or absence, and whether intraparticle diffusion is the adsorption rate–limiting step. There are four stages in the diffusion mechanism:

a. Adsorbate particles migrate from a bulk solution to the adsorbent surface.

b. Diffusion to adsorbent's surface through boundary layer.

c. At a position, adsorption occurs and

d. Intra-particle diffusion in to adsorbent inner [145] .

The equation for intraparticle diffusion is as follows [94] .:

$$q_t = k_{id}t^{1/2} + I \qquad \ldots 4.5$$

(I) which denotes intercept, and K_{id} denotes intraparticle diffusion rate constant (mg g^{-1} $min^{-0.5}$). Only rate limiting factor regulating the system will be is intra-particle diffusion, if intraparticle diffusion happens, so q_t vs $t^{1/2}$ will have been linear, as well as line will pass through the origin point [146] .

If the plots don't really pass through the origin point, these implies that there is some boundary layer controller, showing that intraparticle diffusion wasn't only rate limiting step, as seen in Figure (4.17a-c) **[147]**. Table (4.10) shows the diffusion rate parameters. Table (4.9) shown a calculations. The intra-partical-diffusion model for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint were studied at $C_{\mathbf{0}}$ = 100 mg/L, pH = 3, $V_{\mathbf{solution}}$ = 25 mL Attapulgite dose = (0.1,0.5, and 0.1) g, Flint dose= (0.6,0.3, and 0.4) g respectively, and temperature = 298K.The results in this study show that intraparticle diffusion controls sorption rate, but it's not only rate limiting step of the system.

Table (4.10) show that the correlation coefficient values (R^2) of the pseudo-second-order model were larger than all these of other models, implying that the pseudo-second-order model is better describes the adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint clays and also q_e, (theoretical) values approaches q_e ,(experimental) one.

Table (4.9) The calculations of Cr (III), Cu (II),and Zn (II) ions adsorption onto Attapulgite and Flint clay using an intra-particle diffusion model after applying experimental data.

clays		Metals ions								
		Cr (III)			Cu (II)			Zn (II)		
	Time (min.)	C_e (mg/L)	q_t (mg/g)	$t^{1/2}$ $min^{1/2}$	C_e (mg/L)	q_t (mg/g)	$t^{1/2}$ $min^{1/2}$	C_e (mg/L)	q_t (mg/g)	$t^{1/2}$ $min^{1/2}$
Attapulgite	10	2.6540	24.3365	3.1622	3.4445	4.8277	3.1622	68.8523	7.7869	3.1622
	20	2.5640	24.3590	4.4721	2.3257	4.8837	4.4721	63.3187	9.1703	4.4721
	30	1.8342	24.5414	5.4772	1.9654	4.9017	5.4772	60.8593	9.7851	5.4772
	40	1.8356	24.5411	6.3245	1.9543	4.9022	6.3245	49.1771	12.7057	6.3245
	60	1.9286	24.5178	7.7459	2.0000	4.9023	7.7459	44.8138	13.7965	7.7459
	90	1.7136	24.5715	9.4868	1.9535	4.9023	9.4868	44.7247	13.8188	9.4868
	120	1.5136	24.6216	10.9544	1.9421	4.9028	10.9544	44.6247	13.8438	10.9544
Flint	10	51.5340	2.0194	3.1622	47.7525	4.3539	3.1622	65.1632	2.1772	3.1622
	20	51.4080	2.0246	4.4721	47.3421	4.3881	4.4721	59.0147	2.5615	4.4721
	30	51.4140	2.0244	5.4772	47.3532	4.3872	5.4772	57.7850	2.6384	5.4772
	40	51.3350	2.0277	6.3245	47.3543	4.3871	6.3245	55.3256	2.7921	6.3245
	60	50.6450	2.0654	7.7459	47.4267	4.3811	7.7459	54.0959	2.8690	7.7459
	90	50.8470	2.0480	9.4868	47.2954	4.3920	9.4868	50.4068	3.0995	9.4868
	120	50.242	2.0732	10.9544	47.1384	4.4051	10.9544	50.3257	3.1046	10.9544

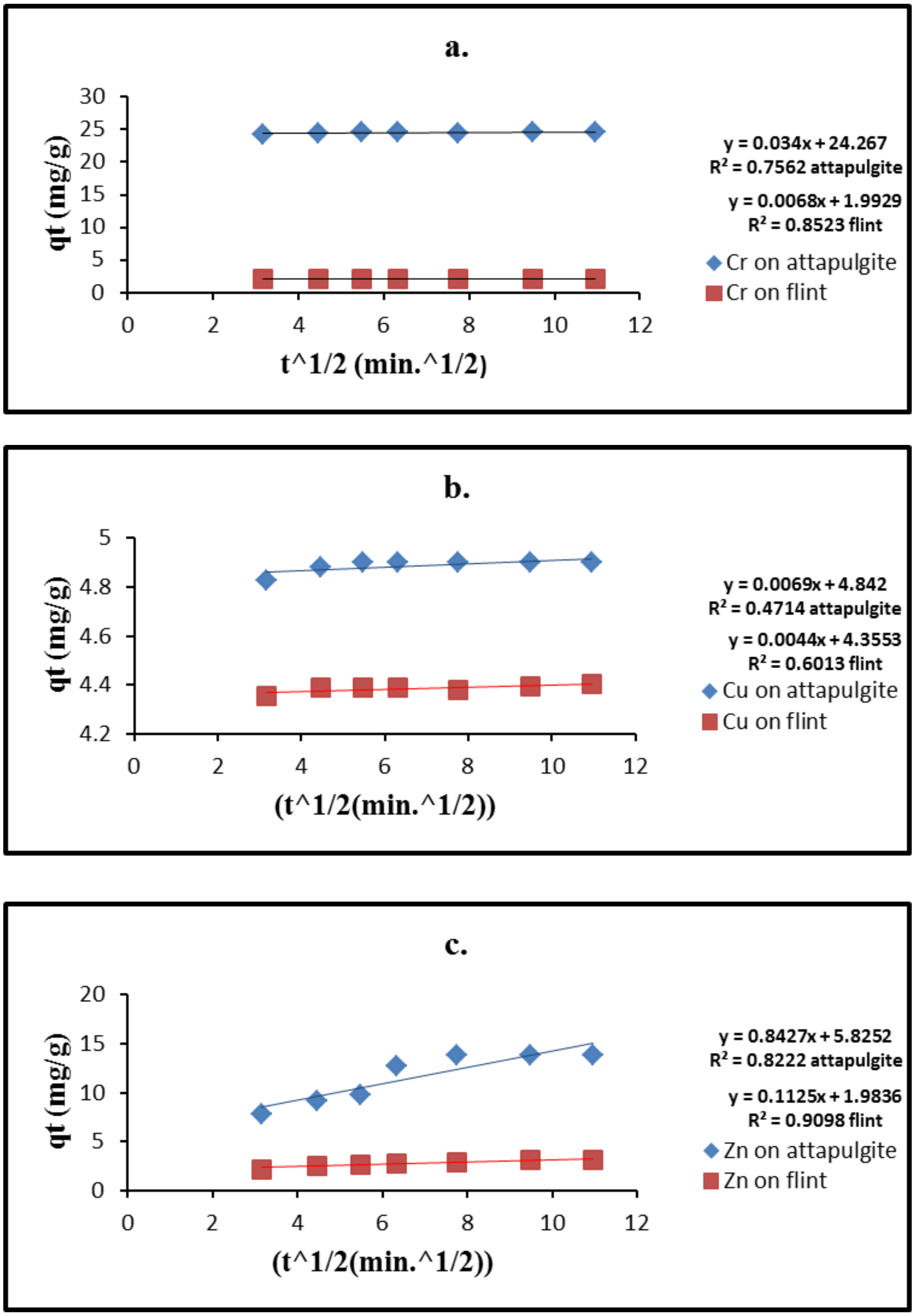


Fig.(4.17a-c) Intra-particle-diffusion model of Cr (III), Cu (II), and Zn (II) ions adsorption on Attapulgite and Flint at C_0 = 100 mg/L, pH = 3, $V_{solution}$ = 25 mL, and temperature = 298K.

Table (4.10) Kinetic parameters of Cr (III), Cu (II), and Zn (II) ions adsorption onto Attapulgite and Flint clays at initial concentration C_0 = 100 mg/L,pH = 3, $V_{solution}$ = 25 mL, partical size of 75 µm, and temperature = 298K.

Clays			**Pseudo first order**			**Pseudo second order**			**Intraparticle diffusion**	
	Metals	**q_e(exp.) mg/g**	**K_1 min^{-1}**	**q_e(cal.) mg/g**	**R^2**	**K_2 g/mg .min**	**q_e(cal.) mg/g**	**R^2**	**K_{id}**	**R^2**
Attapulgite	**Cr (III)**	**24.6216**	**0.0196**	**0.2640**	**0.6674**	**0.9700**	**24.5700**	**1.0000**	**0.0340**	**0.7562**
Flint		**2.0732**	**0.0127**	**0.0620**	**0.6244**	**1.3900**	**2.0620**	**0.9999**	**0.0068**	**0.8523**
Attapulgite	**Cu (II)**	**4.9028**	**0.0560**	**0.0270**	**0.5900**	**3.3200**	**4.9070**	**1.0000**	**0.0069**	**0.4714**
Flint		**4.4051**	**0.0098**	**0.0320**	**0.3623**	**2.1100**	**4.4030**	**1.0000**	**0.0044**	**0.6013**
Attapulgite	**Zn (II)**	**13.8438**	**0.0336**	**4.5160**	**0.3358**	**0.0100**	**15.4560**	**0.9922**	**0.8427**	**0.8222**
Flint		**3.1046**	**0.0158**	**0.6070**	**0.1202**	**0.0500**	**3.2620**	**0.9990**	**0.1125**	**0.9098**

4.4 Adsorption isotherms study

Adsorption isotherms were investigated in order to model adsorption behavior. The equilibrium between the concentration of Cr (III), Cu (II), and Zn (II) ions in the aqueous solution and their concentration on the solid is shown by the adsorption isotherm (q_e , C_e). It is clear that as the equilibrium Cr (III), Cu (II), and Zn (II) ions concentrations increases, so does adsorption capacity. The form of the adsorption isotherms of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint clays, as shown in Figures (4.18a-c and 4.19a-c), was compatible with the S-type on Giles classified (Figure (2.3) in Chapter tow). The values of Cr (III), Cu (II), and Zn (II) ions uptake by two adsorbents are shown in Tables (4.11 and 4.12) (Attapulgite and Flint clays). The Attapulgite had a higher capacity for adsorption of Cr (III), Cu (II), and Zn (II) ions than Flint. According to the results the adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Cr (III) and Zn (III) ions on Flint increased with increasing temperature, suggesting that adsorption is regulated by an endothermic reaction. This might be because increase ions diffuse within the crystal lattice of the clay with the increase of the temperature [140]. On the other hand, the adsorption of Cu (II) ions on Flint clay decreases as the temperature increases, suggesting that adsorption is regulated by exothermic reaction. This might be because when as the temperature increase, the reaction force between copper ions and the active positions on the adsorption surface weakens[141]. These findings may also be due to a different chemical reaction between Attapulgite or Flint clays and Cr (III), Cu (II), and Zn (II) ions, which absorbs or releases a significant amount of energy in order for adsorption to occur [148].

Table (4.11) Adsorption values of Cr (III), Cu (II), and Zn (II) ions on Attapulgite at different temperatures, pH = 3, $V_{solution}$ = 25 mL , particle size of 75 µm , Attapulgite dose = (0.1,0.5, and 0.1) g, contact time on Attapulgite = (30,40, and 90) minutes respectively.

Clay	Metals		Temp. (298K)		Temp.(318K)	
		C_0 mg/L	C_e mg/L	q_e mg/g	C_e mg/L	q_e mg/g
Attapulgite	Cr **(III)**	20	2.7630	4.3092	0.0000	5.0000
		60	4.0780	13.9805	0.0000	15.0000
		100	5.8750	23.5312	0.0530	24.9867
		140	8.9880	32.7530	0.2420	34.9395
		180	17.7040	40.5740	1.8350	44.5412
		220	98.6340	30.3415	27.0430	48.2392
	Cu (II)	20	1.2130	0.9393	0.0000	1.0000
		60	3.0973	2.8451	0.0000	3.0000
		100	18.5432	4.0728	1.0453	4.9477
		140	34.7843	5.2607	20.6858	5.9657
		180	50.2994	6.4850	33.4021	7.3298
		220	56.1047	8.1947	49.6775	8.5161
	Zn (II)	20	3.6643	4.0839	1.8267	4.5433
		60	26.4277	8.3930	19.0495	10.2376
		100	41.7989	14.5502	22.1237	19.4690
		140	71.3139	17.1715	53.9683	21.5079
		180	80.1677	24.9580	66.4277	28.3930
		220	104.7618	28.8095	91.3465	32.1633

Table (4.12) Adsorption values of Cr (III), Cu (II), and Zn (II) ions on Flint at different temperatures, pH =3, $V_{solution}$ = 25 mL , particle size of 75 µm, Flint dose = (0.6,0.3, and 0.4) g, and contact time on Flint = (10,10, and 90) minutes respectively.

Clay	**Metals**		**Temp. (298K)**		**Temp.(318K)**	
		C_0 mg/L	**C_e mg/L**	**q_e mg/g**	**C_e mg/L**	**q_e mg/g**
Flint	Cr **(III)**	**20**	**1.3649**	**0.7764**	**0.0000**	**0.8333**
		60	**18.9329**	**1.7111**	**11.1056**	**2.0372**
		100	**51.6336**	**2.0152**	**43.6323**	**2.3486**
		140	**70.7670**	**2.8847**	**68.9406**	**2.9608**
		180	**85.5519**	**3.9353**	**83.7255**	**4.0114**
		220	**98.6840**	**5.0548**	**96.0756**	**5.1635**
	Cu (II)	**20**	**12.3926**	**0.6339**	**13.4810**	**0.5432**
		60	**26.8265**	**2.7644**	**34.0130**	**2.1655**
		100	**62.7114**	**3.1073**	**67.6014**	**2.6998**
		140	**85.9156**	**4.5070**	**92.1355**	**3.9887**
		180	**109.4130**	**5.8822**	**121.1617**	**4.9031**
		220	**130.4916**	**7.4590**	**140.5125**	**6.6239**
	Zn (II)	**20**	**6.7455**	**0.8284**	**3.7639**	**1.0147**
		60	**25.1980**	**2.1751**	**24.0934**	**2.2441**
		100	**49.7920**	**3.1380**	**34.4229**	**4.0985**
		140	**83.6087**	**3.5244**	**63.9335**	**4.7541**
		180	**120.4998**	**3.7187**	**94.0612**	**5.3711**
		220	**142.0195**	**4.8737**	**119.2701**	**6.2956**

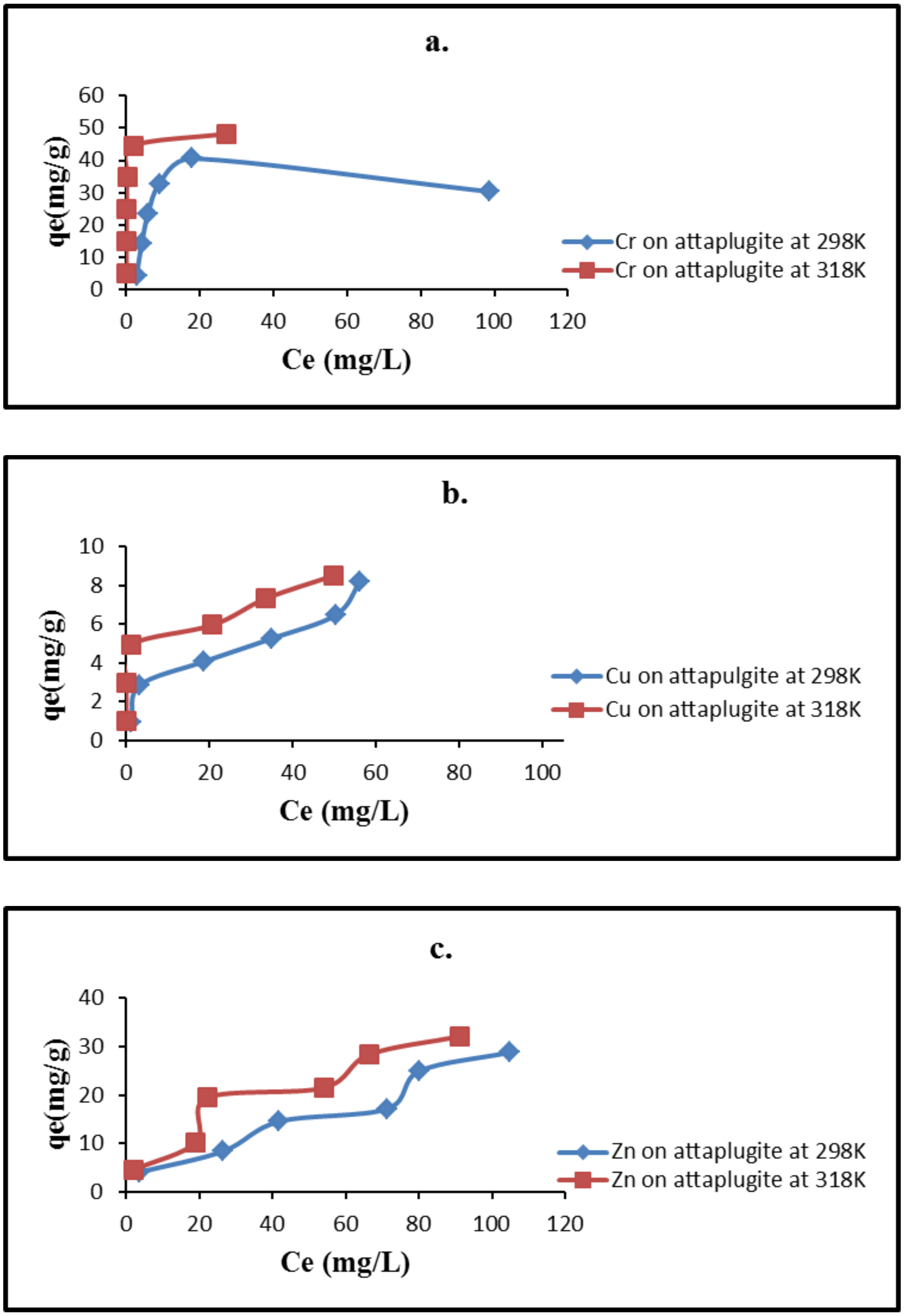


Fig.(4.18 a-c) Adsorption isotherms of Cr (III), Cu (II), and Zn (II) ions on Attapulgite at different temperatures, pH = 3, $V_{solution}$ = 25 mL, Attapulgite dose = (0.1,0.5 and 0.1) g and contact time = (30,40, and 90) minutes respectively.

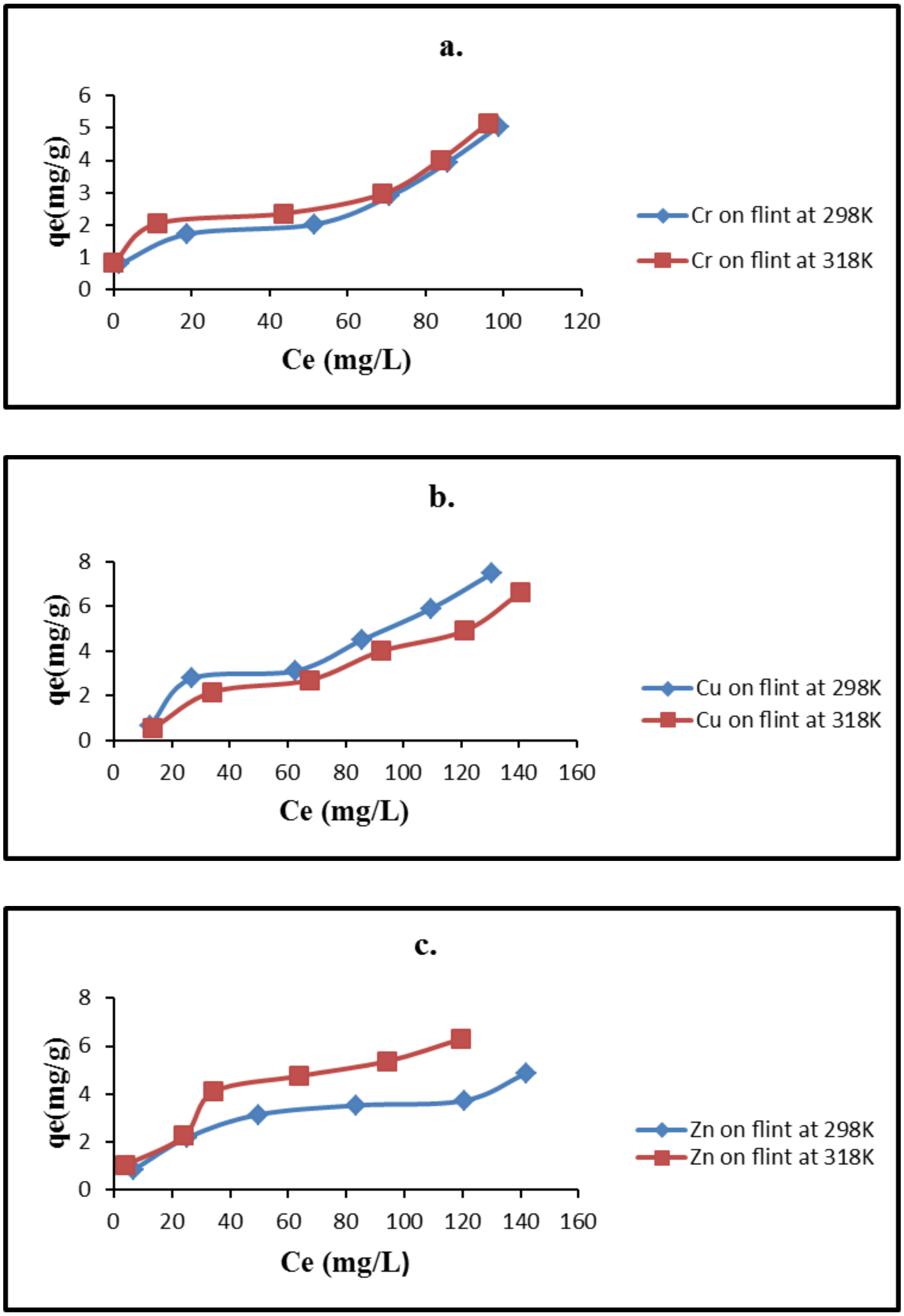


Fig.(4.19a-c) Adsorption isotherms of Cr (III), Cu (II), and Zn (II) ions on Flint at different temperatures, pH = 3, $V_{solution}$ = 25mL, Flint dose = (0.6,0.3 and 0.4) g and contact time = (10,10,and 90) minutes respectively.

As mentioned in (section 2.1.6), many models were developed to describe experimental data of adsorption isotherms. The most commonly used models are Langmuir (section 2.1.6.1), Freundlich (section 2.1.6.2), and D-R (section 2.1.6.3). These three models are presented in this study. The linearized forms (4.6,4.7 and 4.8) are used for Langmuir, Freundlich, and D-R models, respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}} C_e \qquad \ldots 4.6$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \ldots 4.7$$

$$\ln q_e = \ln q_{max} - \beta \varepsilon^2 \qquad \ldots 4.8$$

The plots for Langmuir, Freundlich and D-R linearized equations for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint clays are shown in Figures ((4.20a-c)–(4.25a-c)). The values of K_L and q_{max} (Langmuir model), K_F and n (Freundlich model), and the measured D-R constants (q_{max},) and main free energy (E) for adsorption were calculated from intercept and slope of each linear plot.

Adsorption type is specifies according to main free sorption energy (E) value physisorption (E <16kJ/mol) or chemisorption (E > 16kJ/mol). The main free energy (E) values in this study were between (0.090 to 7.107) kJ/mol, which is classfied as physisorption process [87] .

Adsorption type is specifies according to R_L value irretrievable (R_L = 0), unfavorable ($R_L > 1$), linear ($R_L =1$), and favorable ($0 < R_L < 1$). R_L values in this study were between (0.002 - 0.973), which is classfied as favorable adsorption processes [149] . Tables (4.13,4.14, and 4.15) shown calculations of Cr (III), Cu (II), and Zn (II) ions adsorption respectively. Table (4.16) lists values for all systems. According to the values of the correlation coefficient (R^2), seen in Table (4.16), the Freundlich isotherm seems to be a better fit for all systems except Cr (III) ions on Attapulgite, which seems to be a good fit for Langmuir isotherm. The Langmuir, Freundlich and D-R isotherm parameters for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Flint clays were studied at pH = 3, $V_{\mathbf{solution}}$ = 25 mL, particle size of 75 µm, Attapulgite dose = (0.1,0.5, and 0.1) g, Flint dose = (0.6,0.3, and 0.4) g, and contact time on Attapulgite = (30,40, and 90) minutes, contact time on Flint = (10,10, and 90) minutes respectively.

Table (4.13) The calculations for Cr (III) adsorption onto Attapulgite and Flint clay using the Langmuir, Freundlich, and D-R isotherms models after applying experimental data.

Clay		**Cr (III)**							
	Temp.(K)	**C_0(mg/L)**	**C_e (mg/L)**	**q_e(mg/g)**	**C_e/q_e**	**logC_e**	**logq_e**	**ε^2**	**lnq_e**
Attapulgite	**298**	20	2.7630	4.3092	0.6411	0.4413	0.6344	0.5508	1.4607
		60	4.0780	13.9805	0.2916	0.6104	1.1455	0.2776	2.6376
		100	5.8750	23.5312	0.2496	0.7690	1.3716	0.1426	3.1583
		140	8.9880	32.7530	0.2744	0.9536	1.5152	0.0642	3.4889
		180	17.704	40.5740	0.4363	1.2480	1.6082	0.0174	3.7031
		220	98.6340	30.3415	3.2507	1.9940	1.4820	0.0005	3.4125
	318	20	0.0000	5.0000	0.0000	0.0000	0.6989	0.0000	1.6094
		60	0.0000	15.0000	0.0000	0.0000	1.1760	0.0000	2.7080
		100	0.0530	24.9867	0.0021	-1.2757	1.3977	62.4535	3.2183
		140	0.2420	34.9395	0.0069	-0.6161	1.5433	18.6980	3.5536
		180	1.8350	44.5412	0.0411	0.2636	1.6487	1.3226	3.7964
		220	27.043	48.2392	0.5606	1.4320	1.6834	0.0092	3.8761
Flint	**298**	20	1.3649	0.7764	1.7579	0.1351	-0.1098	1.7440	-0.2530
		60	18.932	1.7111	11.0645	1.2772	0.2332	0.0152	0.5371
		100	51.6336	2.0152	25.6212	1.7129	0.3043	0.0021	0.7007
		140	70.7670	2.8847	24.5317	1.8498	0.4601	0.0011	1.0594
		180	85.5519	3.9353	21.7394	1.9322	0.5949	0.0007	1.3699
		220	98.6840	5.0548	19.5227	1.9942	0.7037	0.0005	1.6203
	318	20	0.0000	0.8333	0.0000	0.0000	-0.0791	0.0000	-0.1823
		60	11.1056	2.0372	5.4512	1.0455	0.3090	0.0519	0.7116
		100	43.6323	2.3486	18.5776	1.6398	0.37081	0.0035	0.8538
		140	68.9406	2.9608	23.2844	1.8384	0.47140	0.0014	1.0854
		180	83.7255	4.0114	20.8717	1.9228	0.6032	0.0009	1.3891
		220	96.0756	5.1635	18.6066	1.9826	0.7129	0.0007	1.6416

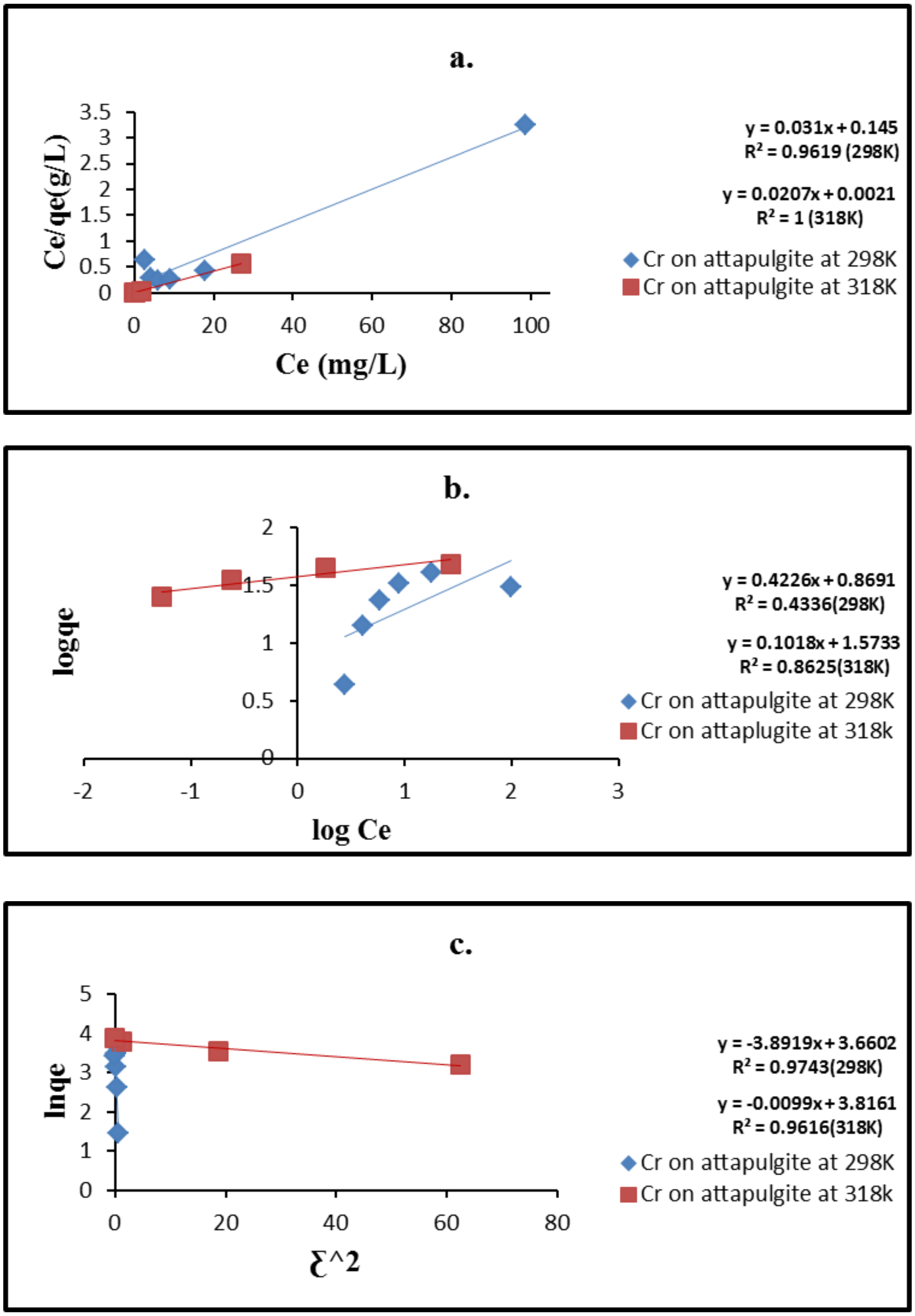


Fig.(4.20 a-c) Linear forms of Langmuir,Freundlich and D-R isotherms for adsorption of Cr (III) ions on Attapugite clay at pH = 3,$V_{solution}$ = 25 mL, Attapulgite dose = 0.1 g, and contact time = 30 minutes.

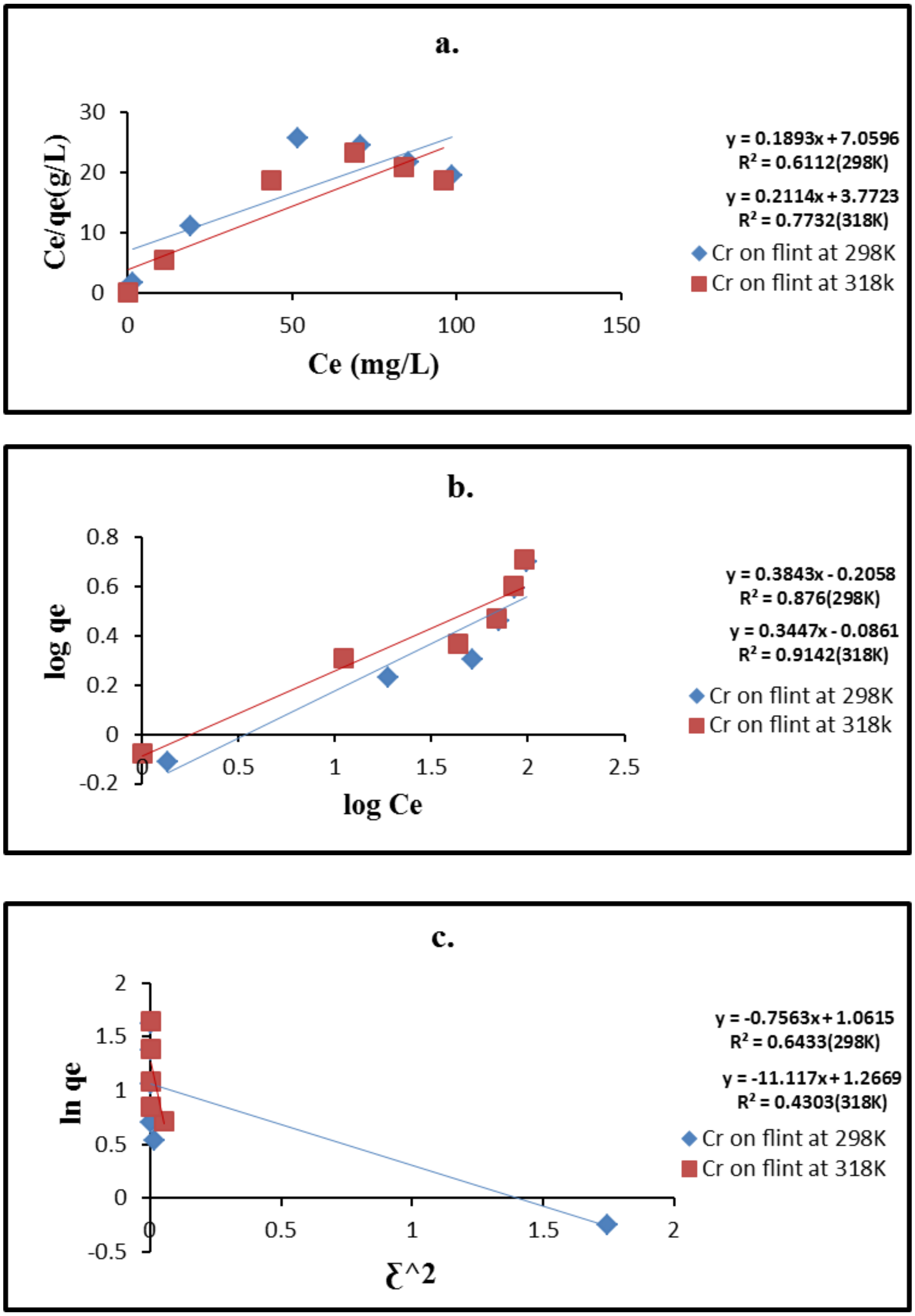


Fig.(4.21 a-c) Linear forms of Langmuir,Freundlich and D-R isotherms for adsorption of Cr (III) ions on Flint clay at pH = 3,$V_{solution}$ = 25 mL, Flint dose = 0.6 g, and contact time = 10 minutes.

Table (4.14) The calculations for Cu (II) adsorption onto Attapulgite and Flint clay using the Langmuir, Freundlich, and D-R isotherms models after applying experimental data

Clay		Cu (II)							
	Temp.(K)	**C_0(mg/L)**	**C_e (mg/L)**	**q_e(mg/g)**	**C_e/q_e**	**logC_e**	**logq_e**	**ε^2**	**lnq_e**
Attapulgite	**298**	20	1.2130	0.9393	1.2913	0.0838	-0.0271	2.0870	-0.0625
		60	3.0973	2.8451	1.0886	0.4909	0.4541	0.4519	1.0456
		100	18.5432	4.0728	4.5528	1.2681	0.6098	0.0159	1.4043
		140	34.7843	5.2607	6.6119	1.5413	0.7210	0.0046	1.6602
		180	50.2994	6.4850	7.7562	1.7015	0.8119	0.0022	1.8694
		220	56.1047	8.1947	6.8464	1.7489	0.9135	0.0018	2.1034
	318	20	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
		60	0.0000	3.0000	0.0000	0.0000	0.4771	0.0000	1.0986
		100	1.0453	4.9477	0.2112	0.0192	0.6944	3.1494	1.5989
		140	20.6858	5.9657	3.4674	1.3156	0.7756	0.0155	1.7860
		180	33.4021	7.3298	4.5569	1.5237	0.8650	0.0060	1.9919
		220	49.6775	8.5161	5.8333	1.6961	0.9302	0.0027	2.1419
Flint	**298**	20	12.3926	0.6339	19.5482	1.0931	-0.1979	0.0347	-0.4557
		60	26.8265	2.7644	9.7041	1.4285	0.4416	0.0077	1.0168
		100	62.7114	3.1073	20.1814	1.7973	0.4923	0.0014	1.1337
		140	85.9156	4.5070	19.0625	1.9340	0.6538	0.0007	1.5056
		180	109.4130	5.8822	18.6005	2.0390	0.7695	0.0004	1.7719
		220	130.4916	7.4590	17.4944	2.1155	0.8726	0.0003	2.0094
	318	20	13.4810	0.5432	24.8154	1.12972	-0.2650	0.0357	-0.6101
		60	34.013	2.1655	15.7061	1.5316	0.3355	0.0058	0.7726
		100	67.6014	2.6998	25.0386	1.8299	0.4313	0.0015	0.9932
		140	92.1355	3.9887	23.0990	1.9644	0.6008	0.0008	1.3834
		180	121.1617	4.9031	24.7107	2.0833	0.6904	0.0004	1.5898
		220	140.5125	6.6239	21.2127	2.1477	0.8211	0.0003	1.8906

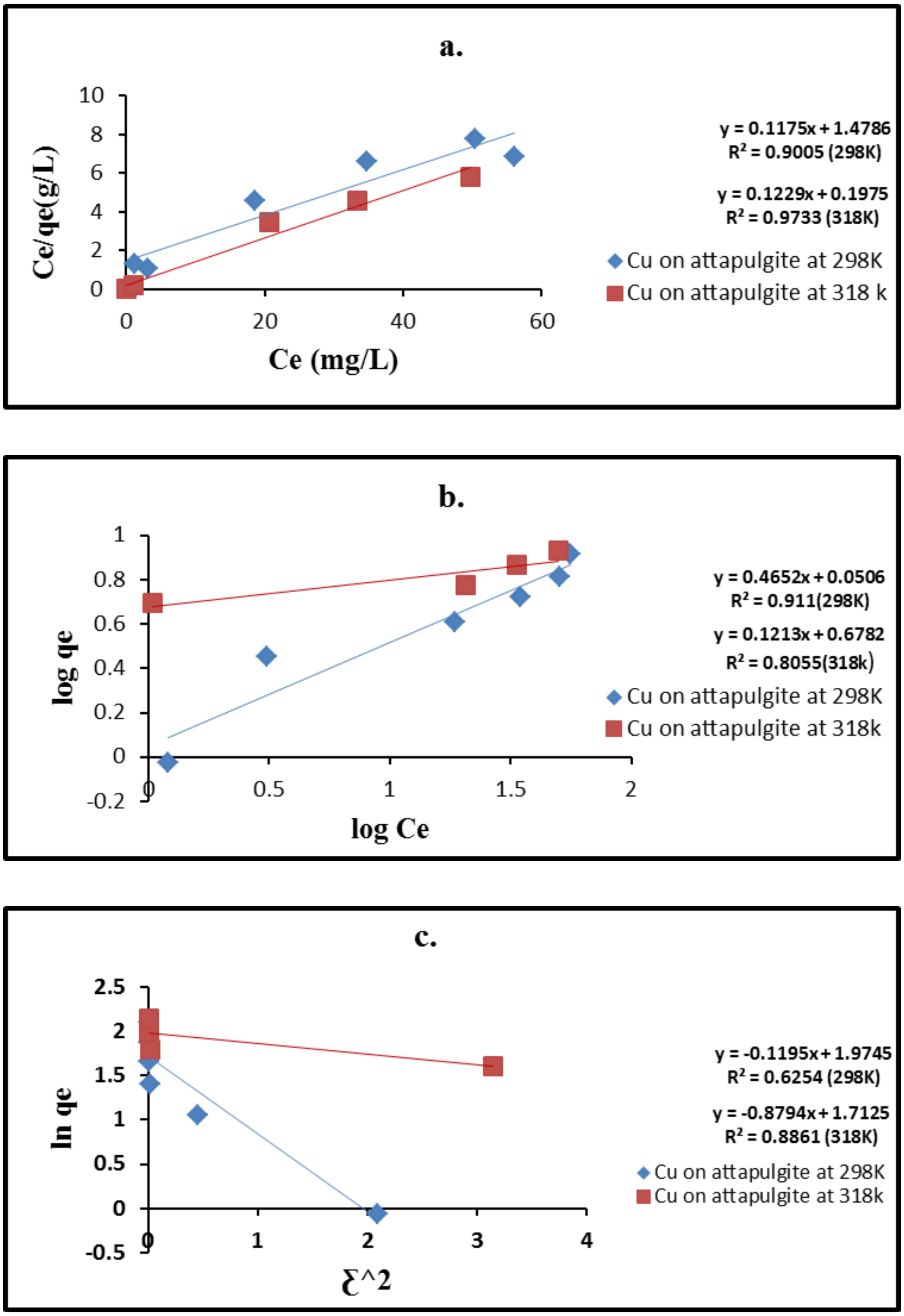


Fig.(4.22 a-c) Linear forms of Langmuir,Freundlich and D-R isotherms for adsorption of Cu (II) ions on Attapulgite clay at pH = 3,$V_{solution}$ = 25 mL, Attapulgite dose = 0.5 g, and contact time = 40 minutes.

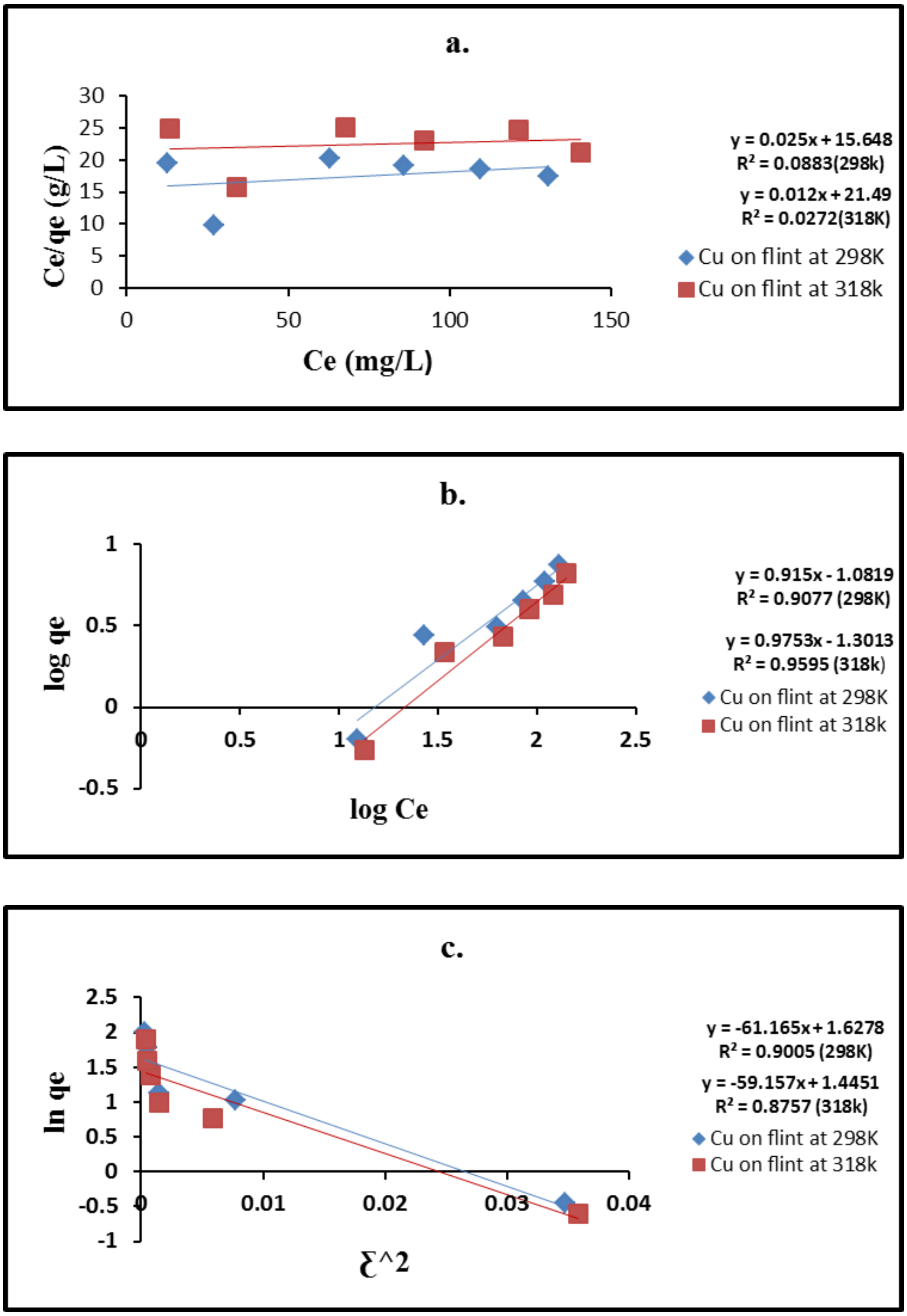


Fig.(4.23 a-c) Linear forms of Langmuir,Freundlich and D-R isotherms for adsorption of Cu (II) ions on Flint clay at pH = 3,$V_{solution}$ = 25 mL, Flint dose = 0.3 g, and contact time = 10 minutes.

Table (4.15) The calculations for Zn (II) adsorption onto Attapulgite and Flint clay using the Langmuir, Freundlich, and D-R isotherms models after applying experimental data.

Clay		Zn (II)							
	Temp.(K)	**C_0(mg/L)**	**C_e (mg/L)**	**q_e(mg/g)**	**C_e/q_e**	**logC_e**	**logq_e**	**ε^2**	**lnq_e**
Attapulgite	**298**	20	3.6643	4.0839	0.8972	0.5639	0.6110	0.3361	1.4070
		60	26.4277	8.3930	3.14875	1.4220	0.9239	0.0079	2.1274
		100	41.7989	14.5502	2.8727	1.6211	1.1628	0.0032	2.6776
		140	71.3139	17.1715	4.1530	1.8531	1.2348	0.0011	2.8432
		180	80.1677	24.9580	3.2120	1.9039	1.3972	0.0008	3.2171
		220	104.7618	28.8095	3.6363	2.0202	1.4595	0.0005	3.3607
	318	20	1.8267	4.5433	0.4020	0.2616	0.6573	1.3323	1.5136
		60	19.0495	10.2376	1.8607	1.2798	1.0101	0.0182	2.3260
		100	22.1237	19.4690	1.1363	1.3448	1.2893	0.0136	2.9688
		140	53.9683	21.5079	2.5092	1.7321	1.3325	0.0023	3.0684
		180	66.4277	28.3930	2.3395	1.8223	1.4532	0.0015	3.3461
		220	91.3465	32.1633	2.8400	1.9606	1.5073	0.0008	3.4708
Flint	**298**	20	6.7455	0.8284	8.1427	0.8290	-0.0817	0.1103	-0.1882
		60	25.1980	2.17512	11.5846	1.4013	0.3374	0.0087	0.7770
		100	49.7920	3.1380	15.8674	1.6971	0.4966	0.0022	1.1435
		140	83.6087	3.5244	23.7224	1.9222	0.5470	0.0008	1.2597
		180	120.4998	3.7187	32.4031	2.0809	0.5703	0.0003	1.3133
		220	142.0195	4.8737	29.1394	2.1523	0.6878	0.0002	1.5838
	318	20	3.7639	1.0147	3.7092	0.5756	0.0063	0.3880	0.0146
		60	24.0934	2.2441	10.7360	1.3818	0.3510	0.0115	0.8083
		100	34.4229	4.0985	8.3987	1.5368	0.6126	0.0057	1.4106
		140	63.9335	4.7541	13.4479	1.8057	0.6770	0.0016	1.5590
		180	94.0612	5.3711	17.5122	1.9734	0.7300	0.0007	1.6810
		220	119.2701	6.2956	18.9449	2.0765	0.7990	0.0004	1.8398

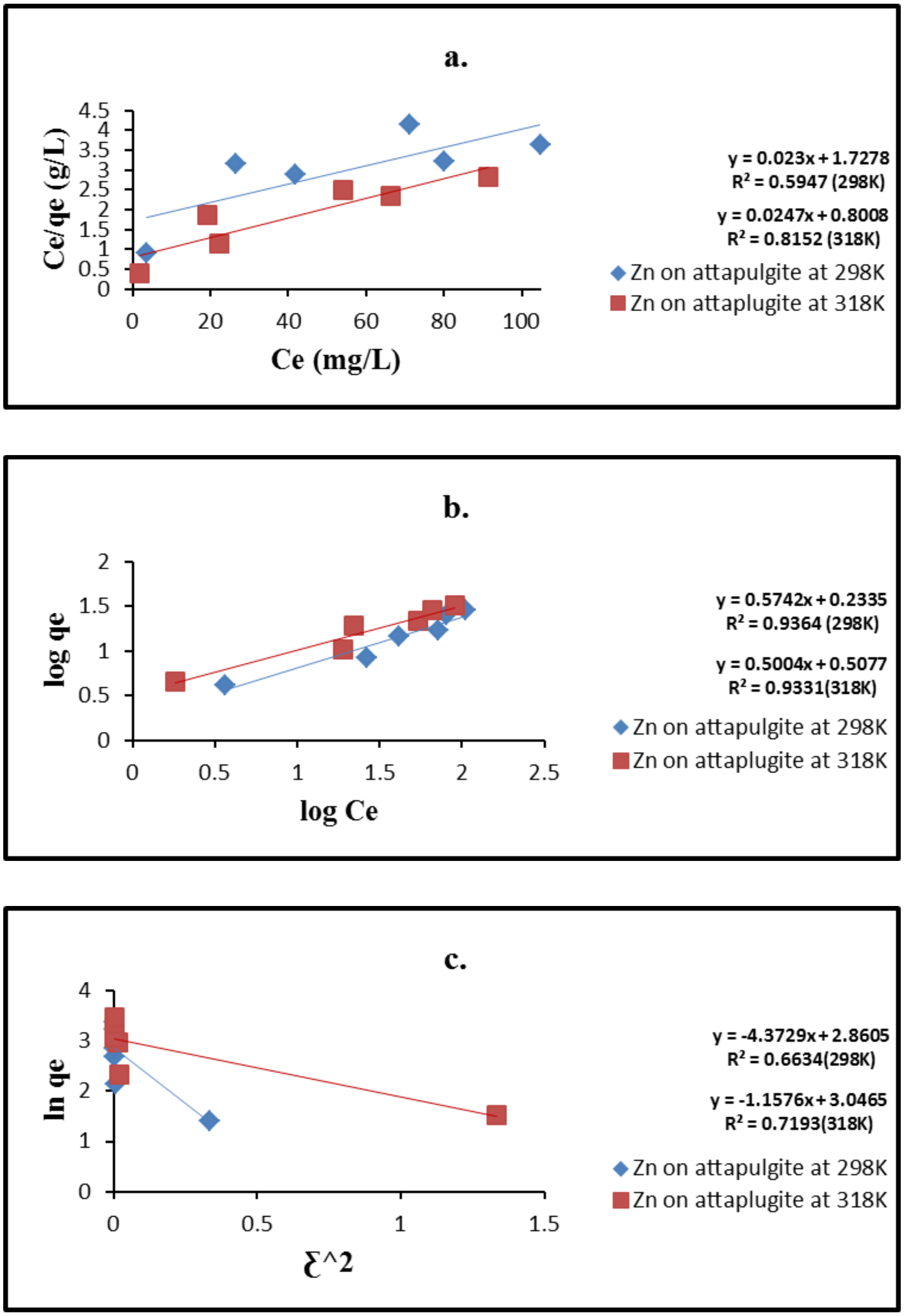


Fig.(4.24 a-c) Linear forms of Langmuir Freundlich and D-R isotherms for adsorption of Zn (II) ions on Attapulgite clay at pH = 3,$V_{solution}$ = 25 mL, Attapuligite dose = 0.1 g, and contact time = 90 minutes.

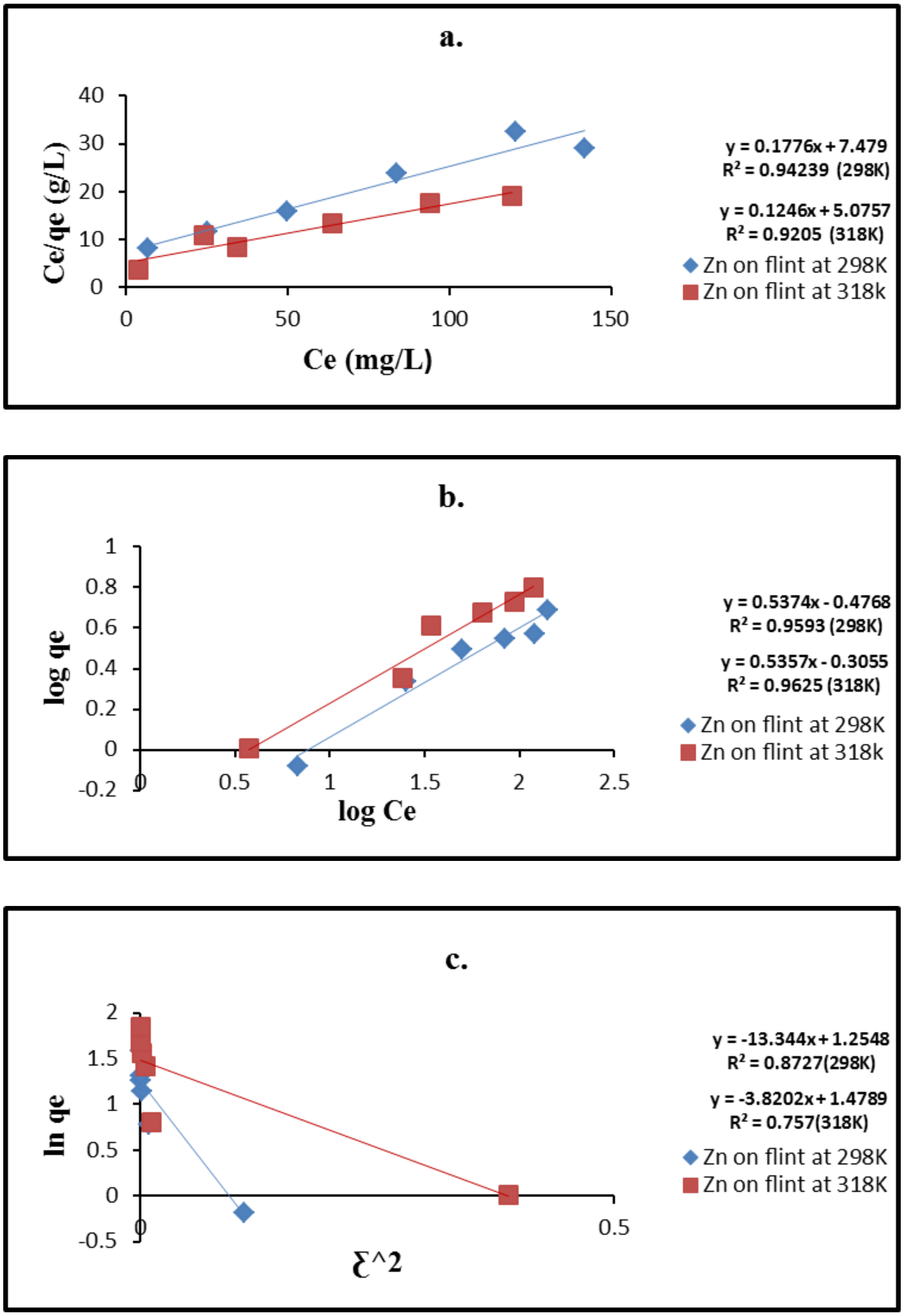


Fig.(4.25 a-c) Linear forms of Langmuir,Freundlich, and D-R isotherms for adsorption of Zn (II) ions on Flint clay at pH = 3,$V_{solution}$ = 25 mL, Flint dose = 0.4 g, and contact time = 90 minutes.

Table (4.16) Langmuir,Freundlich, and D-R isotherms factors for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapugite and Flint clays at pH = 3, $V_{solution}$ = 25 mL , particle size of 75 µm,

Clays				**Langmauir**			**Freundlich**			**D-R**			
	Metals	**Temp. K**	**q_{max} mg/g**	**K_L L/mg**	**R_L**	**R^2**	**n**	**K_F L/g**	**R^2**	**β mol^2/KJ^2**	**q_{max} mg/g**	**E KJ/mol**	**R^2**
Attapulgite	**Cr^{3+}**	298	32.258	0.214	0.045	0.9619	2.366	7.398	0.4336	3.8920	38.869	0.358	0.9743
		318	48.309	9.857	0.001	1.000	9.823	37.437	0.8625	0.0100	45.427	7.107	0.9616
Flint		298	5.283	0.027	0.272	0.6112	2.602	0.623	0.8760	0.7560	2.891	0.831	0.6433
		318	4.730	0.056	0.151	0.7732	2.901	0.820	0.9142	11.1170	3.550	0.212	0.4303
Attapulgite	**Cu^{2+}**	298	8.511	0.079	0.112	0.9005	2.150	1.124	0.911	0.1200	7.203	2.046	0.6254
		318	8.137	0.622	0.016	0.9733	8.244	4.767	0.8055	0.8790	5.543	0.754	0.8861
Flint		298	40.000	0.002	0.862	0.0883	1.093	0.083	0.9077	61.1650	5.093	0.090	0.9005
		318	83.333	0.001	0.947	0.0272	1.025	0.050	0.9595	59.1570	4.242	0.092	0.8757
Attapulgite	**Zn^{2+}**	298	43.478	0.013	0.245	0.5947	1.742	1.712	0.9364	4.3730	17.470	0.338	0.6634
		318	40.486	0.031	0.429	0.8152	1.998	3.219	0.9331	1.1580	21.042	0.657	0.7193
Flint		298	5.631	0.024	0.289	0.9423	1.861	0.334	0.9593	13.3440	3.507	0.194	0.8727
		318	8.026	0.025	0.296	0.9205	1.867	0.495	0.9625	3.8200	4.388	0.362	0.757

4.5 Thermodynamics parameters study

The Langmuir constant (K_L) is linked to energy of the adsorption process. The Langmuir model assumes that adsorption is confined to a single monolayer. Adsorption from a solution to a solid can be viewed as a two-dimensional ideal solution of solvent and solute molecules, with the solute and solvent competing for active positions on the adsorbent surface [22] . The current equilibrium constant for the adsorption process, K, is related to K_L and the concentration of water in aqueous solution, C (55.56 mole/L), which is clearly constant in dilute solutions. As a result, K can be calculated using the equation [95,151] .

$$\boldsymbol{K = CK_L} \qquad \ldots \mathbf{4.9}$$

Equation (4.9) can be used to obtain k values by using the K_L (L/mg) values in Table (2) and applying the following equation:

$$\boldsymbol{K = 1000K_L \times M.W_t\ of\ adsorbate \times 55.56} \qquad \ldots \mathbf{4.10}$$

Also, can be calculated equilibrium constant (K) from Freundlich constant (K_F) using the next equation[95].

$$\boldsymbol{K = K_F \rho \left(\frac{10^6}{\rho \times M.W_t of\ adsorbate}\right)^{\left(1-\frac{1}{n}\right)}} \qquad \ldots \mathbf{4.11}$$

Where as ρ is the density of pure water (g/mL) (assumed as ≈1.0 g/mL)

The thermodynamic parameters ($\Delta G°$, $\Delta H°$,and $\Delta S°$) can thus be determined using the following thermodynamic equations [95,151,and 135].:

$$\boldsymbol{\Delta G° = -RT \ln K} \qquad \ldots \mathbf{4.12}$$

$$\boldsymbol{\Delta G° = \Delta H° - T\Delta S°} \qquad \ldots \mathbf{4.13}$$

$$\ln\frac{K_2}{K_1}=\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\qquad \ldots 4.14$$

All thermodynamic parameters values that calculated in this study were shown in Table (4.17) Commonly, physisorption has a free energy change of (-80 to 0) KJ mol^{-1}, while chemisorption has a free energy change of (-400 to -80) KJmol^{-1} **[45,152,153,and 135]**. The values of the change in (ΔG°) were within between (-45.3780 to 4.1313) KJmol^{-1} at all measured temperatures, indicating that the adsorption process was physisorption. The values of (ΔG°) of Cr (III, Cu (II), and Zn (II) ions adsorption on Attapulgite and of Cr (III) and Zn (II) ions adsorption on Flint were negative, suggesting a spontaneous adsorption process. In contrast, the values of (ΔG°) of Cu (II) ions adsorption on Flint clay were positive, suggesting a non-spontaneous adsorption process.The enthalpy values (ΔH°) of Cr (III), Cu (II), and Zn (II) ions adsorption on Attapulgite and of Cr (III) and Zn (II) ions adsorption on Flint were positive, suggesting an endothermic adsorption process. In contrast, the enthalpy values (ΔS°) of Cu (II) ions adsorption on Flint clay were negative, suggesting an exothermic adsorption process. The entropy values (ΔS°) of Cr (III), Cu (II), and Zn (II) ions adsorption on Attapulgite and of Cr (III) and Zn (II) ions adsorption on Flint were positive, suggesting an increase randomness. In contrast, the entropy values (ΔH°) of Cu (II) ions adsorption on Flint clay were negative, suggesting a decrease randomness. As shown in Table(4.17). Thermodynamic functions for adsorption of Cr (III), Cu (II), and Zn (II) ions on Aattapugite and Flint clays were studied at pH = 3, $V_{solution}$ = 25 ml, particle size of 75 μm, Attapulgite dose = (0.1,0.5, and 0.1) g, Flint dose = (0.6,0.3, and 0.4) g respectively, and contact time on Attapulgite = (30,40, and 90) minutes, contact time on Flint = (10,10, and 90) minutes respectively.

Table (4.17) Thermodynamic functions for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapugite and Flint clays at pH =3, $V_{solution}$ = 25 mL ,and particle size of 75 µm.

Clays	Metals	T (K)	1/T	K	lnK	ΔGº KJ/mol	ΔHº KJ/mol	ΔSº J/mol.K
Attapulgite	Cr^{3+}	298	0.0033	617006.9	13.3326	-33.0326	150.9138	617.2698
		318	0.0031	28447714	17.1635	-45.378		
Flint		298	0.0033	271.2876	5.6031	-13.8823	25.9785	133.7611
		318	0.0031	524.6040	6.2626	-16.5575		
Attapulgite	Cu^{2+}	298	0.0033	280264.7	12.5432	-31.0774	81.0733	376.3449
		318	0.0031	2194654	14.6015	-38.6043		
Flint		298	0.0033	0.1887	-1.6675	4.1313	-42.8065	-157.51
		318	0.0031	0.0636	-2.7541	7.2815		
Attapulgite	Zn^{2+}	298	0.0033	103.7825	4.6422	-11.5016	52.9612	216.3185
		318	0.0031	398.1058	5.9867	-15.828		
Flint		298	0.0033	86166.28	11.3640	-28.1552	1.3082	98.8706
		318	0.0031	89075.85	11.3972	-30.1326		

4.6 Application of optimum conditions

After adjusting all the optimum conditions (pH, adsorbent amount, contact time, and temperature) for adsorption of heavy metals Cr (III), Cu (II), and Zn (II) ions in monosystem onto Attapulgite and Flint clays from batch experiments onto synthetic water as shown in table (4.18). The optimal conditions were applied on the ternary heavy metals ions mixture and the Al-Quds power station wastewater sample.

Table (4.18) Optimum conditions used for batch experiments on synthetic water .

Clays	metals	Inaitial conc.(mg/l)	Optimum conditions			
			Contact time (min.)	Clay dosage(g)	pH	Temperature (K)
Attapulgite	Cr^{3+}	100	30	0.1	5	328
	Cu^{2+}	100	40	0.5	5	328
	Zn^{2+}	100	90	0.1	4	328
Flint	Cr^{3+}	100	10	0.6	5	328
	Cu^{2+}	100	10	0.3	5	298
	Zn^{2+}	100	90	0.4	4	328

4.6.1 Application of optimum conditions on synthetic ternary heavy metals mixture

Standard stock solutions of heavy metals were used to prepare a ternary mixture solution (100 mg/L) from Cr (III), Cu (II), and Zn (II) ions. Then, using the batch method, optimal conditions were applied to a ternary mixture solution. The results showed that the removal percentage on Attapulgite was perfect and followed the order (Cr (III) > Cu (II) > Zn (II)). while the removal percentage on Flint was lower and followed the order (Zn (II) > Cu (II) > Cr (III)). As a result, the Attapulgite clay shows removal efficiency higher than Flint clay.As seen in Table (4.19).

Table (4.19) Results of optimum conditions on synthetic ternary heavy metals mixture.

Clays	Metals	Initial Conc.(mg/l)	Final Conc.(mg/l)	Removal %	Optimum conditions			
					Contact time(min.)	Clay dosage(g)	pH	Temperature (K)
Attapulgite	Cr^{3+}	100	0.00	100	30	0.1	5	328
	Cu^{2+}	100	0.156	99.85	40	0.5	5	328
	Zn^{2+}	100	0.319	99.68	90	0.1	4	328
Flint	Cr^{3+}	100	71.86	28.13	10	0.6	5	328
	Cu^{2+}	100	63.45	36.54	10	0.3	5	298
	Zn^{2+}	100	24.69	75.30	90	0.4	4	328

4.6.2 Application of optimum conditions on the Al-Quds power station wastewater sample.

Using the batch method, optimal conditions were applied to a Al-Quds power station wastewater sample. The results showed that the removal percentage on Attapulgite was perfect and followed the order (Cr (III) > Cu (II) > Zn (II)). While, the removal percentage on Flint was lower and followed the order (Zn (II) > Cu (II) > Cr (III)). As a result, the Attapulgite clay shows removal efficiency higher than Flint clay. As shown in Table (4.20).

Table (4.20) Results of optimum conditions on Al-Quds power station wastewater sample.

Clays	Metals	Initial conc.(mg/l)	Final conc.(mg/l)	Removal %	Optimum conditions			
					Contact time(min.)	Clay dosage(g)	pH	Temperature (K)
Attapulgite	Chromium	76.09	0.00	100	30	0.1	5	328
	Copper	97.39	0.321	99.67	40	0.5	5	328
	Zinc	63.97	0.521	99.18	90	0.1	4	328
Flint	Chromium	76.09	55.78	26.69	10	0.6	5	328
	Copper	97.39	58.59	39.83	10	0.3	5	298
	Zinc	63.97	17.83	72.08	90	0.4	4	328

4.7 Conclusion

1- The main objective of this study was to look into the viability of using Attapulgite and Flint clays as adsorbents for removal of industrial wastewater harmful metals such as Cr (III), Cu (II), and Zn (II) ions. The adsorption capacity of Attapulgite for heavy metals Cr (III), Cu (II), and Zn (II) ions was greater than that of Flint clay. The equilibration time for adsorption of Cr (III), Cu (II), and Zn (II) ions by Attapulgite and Flint clays was between (10 to 90) minutes. The best adsorption of Zn (II) ion occurred at pH = 4, whereas the adsorption of Cr (III) and Cu(II) ions increased as pH increased.

2- The experimental results were quite consistent with pseudo-second-order kinetic model and also with the simple external and intra-particle model.

3- The experimental results at two temperatures (298 and 318) K for the Attapulgite and Flint for removal of Cr (III), Cu (II), and Zn (II) ions were fitted to Freundlich isotherm, but the Cr (III) ion on Attapulgite, which was fitted to Langmuir isotherm model.

4- Negative values of ΔG^o for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Cr (III) and Zn (II) on Flint suggest that a spontaneous system. In contrast, positive ΔG^o values for adsorption of Cu (II) on Flint clay, suggest that a non-spontaneous system. Positive values of ΔS° and ΔH° for adsorption of Cr (III), Cu (II), and Zn (II) ions on Attapulgite and Cr(III) and Zn (II) on Flint suggest that randomness-increasing and an endothermic system. On the other hand, Negative ΔS° and ΔH° values for adsorption of Cu (II) on Flint clay, suggest a randomness-decreasing and an exothermic system.

4.8 Future work

1- The study of influencing factors, kinetics, and isotherms models for heavy metal adsorption using Attapulgite clay as an adsorbent surface in a ternary system. due to its high efficiency when used in the mono-system in the current study.

2- Studying the possibility of modifying the surface of Flint clay to increase its efficiency in removing heavy elements and making it more susceptible to inorganic materials using other compounds.

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الخلاصة

تناولت هذه الرسالة دراسة استخدام اطيان عراقية هي الاتبلغايت والفلنت كسطوح مازة رخيصة ومتوفرة وصديقة للبيئة لإزالة المعادن الثقيلة (الكروم ،النحاس ،الزنك) من مياه الصرف الصناعية. حيث درس تأثير زمن الاتزان ، وجرعة الطين ، والدالة الحامضية ، ودرجة الحرارة على امتزاز أيونات الكروم الثلاثي والنحاس الثنائي والزنك الثنائي (Cr^{+3}، Cu^{+2}، Zn^{+2}) على اطيان الاتبلغايت والفلنت من محاليلها المصنعة في النظام الأحادي بطريقة الدفعات ثم تم تحديد الظروف المثالية من تجارب الامتزاز وتطبيقها على عينة مياه الصرف الصناعي. حيث أظهرت النتائج أن طين الاتبلغايت له كفاءة إزالة أعلى من طين الفلنت ، وقدرة الامتزاز القصوى للأيونات (الكروم ، النحاس، الزنك) على طين الاتبلغايت تتبع الترتيب (الكروم > النحاس > الزنك) بينما على طين الفلنت تتبع الترتيب (الزنك > النحاس > الكروم). كان للدالة الحامضية تأثير ملحوظ على امتزاز أيونات (الكروم ، النحاس، الزنك) في كلا النظامين حيث زاد امتزاز أيونات (الكروم ، النحاس) مع زيادة الدالة الحامضية في حين أن أفضل امتزاز لأيون (الزنك) كان عند الدالة الحامضية (4) . تم وصف البيانات الحركية باستخدام نماذج الحركية من المرتبة الأولى والثانية الكاذبة ونموذج الحركية للانتشار داخل الجسيمات حيث توافقت النتائج التجريبية مع نموذج المرتبة الثانية الكاذبة و نموذج الانتشار داخل الجسيمات.

طبقت نماذج ايزوثيرمات الحرارة لانكماير وفريندلج وودوبنين رادوشيفك على النتائج التجريبية لامتزاز أيونات (الكروم ، النحاس، الزنك) على اطيان الاتبلغايت والفلنت عند درجتي حرارة (298 و 318 كلفن). حيث توافقت كل النتائج مع نموذج فريندلج ماعدا امتزاز ايون الكروم على الاتبلغايت توافق مع نموذج لانكماير.

تم حساب دوال الديناميكية الحرارية مثل التغير في الطاقة الحرة القياسية (كبس) ΔG°، والتغير في المحتوى الحراري القياسي ΔH° ،والتغير في الانتروبيي القياسي ΔS° باستخدام معادلات فانت هوف لامتزاز ايونات (الكروم ، النحاس، الزنك) على اطيان الاتبلغايت والفلنت.

قيم التغير في الطاقة الحرة ΔG° لامتزاز أيونات الكروم والنحاس والزنك على الاتبلغايت وامتزاز أيونات الكروم والزنك على الفلنت كانت سالبة، مما يشير إلى ان عملية الامتزازتلقائية. في

حين كانت قيم التغير في الطاقة الحرة ΔG° لامتزاز أيون النحاس على طين الفلنت موجبة، مما يشير إلى ان عملية الامتزاز غير تلقائية. من جانب اخر تراوحت قيم التغير في الطاقة الحرة ΔG° بين (45.378- إلى4.1313) كيلو جول لكل مول في جميع درجات الحرارة المقاسة ، مما يشير إلى أن عملية الامتزاز فيزيائية.

قيم التغير في المحتوى الحراري ΔH° لامتزاز أيونات الكروم والنحاس والزنك على الاتبلغايت وامتزاز أيونات الكروم والزنك على الفلنت كانت موجبة، مما يشير إلى ان عملية الامتزاز ماصة للحرارة. في حين كانت قيم المحتوى الحراري ΔH° لامتزاز أيون النحاس على طين الفلنت سالبة، مما يشير إلى ان عملية الامتزاز طاردة للحرارة.

قيم التغير في الانتروبيي ΔS° لامتزاز أيونات الكروم والنحاس والزنك على الاتبلغايت وامتزاز أيونات الكروم والزنك على الفلنت كانت موجبة مما يشير إلى زيادة العشوائية في حين كانت قيم الانتروبيي ΔS° لامتزاز أيونات النحاس على طين الفلنت سالبة مما يشير إلى انخفاض العشوائية.

طبقت الظروف المثالية المتحققة من تجارب الامتزاز على عينة مياه الصرف الصناعي المأخوذة من محطة كهرباء القدس حيث أظهرت النتائج أن نسبة الإزالة بواسطة طين الاتبلغايت كانت جيدة وتتبع الترتيب (الكروم > النحاس > الزنك) في حين كانت نسبة الإزالة بواسطة طين الفلنت أقل وتتبع الترتيب (الزنك > النحاس > الكروم) وعليه فان طين الاتبلغايت له كفاءة إزالة أعلى من طين الفلنت ويمكن استخدامه في معالجة المياه الملوثة صناعيا بالعناصر التي كانت قيد الدراسة في العديد من المجالات الصناعية وخاصة معامل الطلاء الكهروكيميائي.

وزارة التعليم العالي والبحث العلمي
جامعـــــــة ديالى
كليـــــــة العلوم
قسم الكيميـــــــاء

معالجة المياه الملوثة صناعيا بتقنية الامتزاز باستخدام بعض الاطيان العراقية

رسالة مقدمة الى
مجلس كلية العلوم / جامعة ديالى
وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء
من قبل الطالب

سلام محمد مالح

بكالوريوس في علوم الكيمياء 2001
جامعة بغداد

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