



REMOVAL OF CADMIUM (CD²⁺) AND LEAD (PB²⁺) FROM AQUEOUS SOLUTION BY ADSORPTION ON A MODIFIED CLAY, KINETIC AND THERMODYNAMIC STUDIES

Dulail Nasir
Hassan Algabary*

Department of Chemistry, Faculty of Science, Al-Baha University *Corresponding Author

Elbasheer HZE

Department of Chemistry, Turaba University College, Taif University

ABSTRACT The montmorillonite clay was modified as an adsorption material to remove Cd²⁺ and Pb²⁺ as inorganic pollutants in the wastewater. The characteristics of adsorbents were evaluated by X-ray Fluorescence (XRF), X-ray diffraction (XRD) patterns, Fourier-transform infrared spectroscopy (FTIR) and Thermogravimetric Analysis (TGA). Additionally, the impact of different parameters such as pH, contact time, adsorbent dosage, type of treatment and solution temperature were studied. The experimental data was investigated by two models kinetically of pseudo-first-order and pseudo-second-order. The results indicated that the adsorption followed pseudo-second-order model with correlation R² = 0.9995 and 0.9473 for Pb²⁺, Cd²⁺ respectively. The equilibrium time of heavy metals was obtained after 4h. The thermodynamic parameters indicated that adsorption of Pb²⁺ on modified clay was exothermic and spontaneous, while endothermic adsorption in Cd²⁺ adsorption case. The characteristic of the method, such as the adsorbent abundance and speed of the adsorption process was effective to remove of pollutants from wastewater.

KEYWORDS : Wastewater, Montmorillonite Clay, Heavy Metals, Pseudo-order

1. INTRODUCTION

Heavy metals are the elements that have a density of more than 5 g/cm³. It considered significant wastewater contaminants that harm people and the environment. Some of heavy metals that classified as priority metals for their high toxicity, despite their toxicity, they are essential for most economic activities such as cadmium, and lead. The source of heavy metals is polluted soil, groundwater and surface water continuously from industry and mining, which affect the ecosystem even if they are in small quantities [1]. Heavy metals unlike organic toxicants do not affected by biodegradation. Cadmium, copper and cobalt are toxic heavy metals that can be introduced into the environment through the agricultural application of sewage sludge, fertilizers, land that contaminated by municipal, and industrial wastes [2-3]. Heavy metal contamination can be found in waste effluents from a variety of Industrial activities, including metal plating, tanneries, mining operations, manufacturing paints, ceramic painting, catalysts, galvanizing iron, alloy industries, polymer stabilizer, wood preservation, storage battery manufacturing, pesticides, pigment factories, and family cloth painting [4-5]. Water containing heavy metal contamination lead to infectious diseases like typhoid and cholera. If contaminated water is consumed on a frequent basis, it might harm the human heart and kidneys. Poor blood circulation, skin sores, vomiting, and nervous system impairment are some of the other health issues linked to contaminated water, indeed, water contamination is claimed to be the largest cause of death for humans all over the world [6-7]. The major pollution of water via harmful chemicals includes heavy metal contaminations such as Mercury, Cadmium, Lead, Chrome and other metals leads to increasing the concentration in drinking water which reaches one millionth, these contaminations result in pathological changes in blood, liver, lung, hair, and other organs. Furthermore, they will also enter the soil in various ways. Cadmium is a known human carcinogen that can cause lung disease, bone lesions, and high blood pressure [8]. The detection of trace and heavy metal contamination in wastewater is a critical step in protecting human and environmental health. Different countries control wastewater in different ways, but the goal is to reduce pollution in natural rivers [9]. Inorganic techniques such as ICP-MS, ICP-OES, FAAS and GFAAS or ETAAS, and can be used to measure trace elements in wastewater [10-11].

Industrial wastewater treatment processes were classified into chemical, physical, and biological processes [12]. There are many techniques that are used to treat wastewater, such as membrane filtration, activated carbon adsorption, advanced oxidation processes [13-14], photocatalysis technology [13] incineration at high temperature, chlorination [12], ion exchange, Fenton reaction, precipitation, combined ultrasound-ozone, ultra-filtration, packed columns [15-16], electro-coagulation [9], solvent extraction, reverse osmosis, adsorption [3], etc. The adsorption appears to be the most successful of these techniques, particularly for effluents with moderate and low concentrations, when using the adsorption method to remove

pollutants, the cost of the adsorbent, environmental availability, and adsorptive properties must be taken into consideration [3,17]. Thajeel [18] studied the adsorption isotherms, kinetics, and thermodynamics of uptake of Fe³⁺, Cu²⁺, Pb²⁺ and Zn²⁺ ions by activated carbon derived from rice husk. Momčilović et al [19] studied the influence of important parameters including pH, initial concentration of Pb ions, contact time, and adsorbent dosage on the removal efficiency in a batch process mode. Investigated the ability of the activated carbon to remove Ni(II), Co(II), Cd(II), Cu(II), Pb(II), Cr(III) and Cr(VI) ions from aqueous solutions by adsorption. Kırbıyık et al. [20] compared the performance of Fe(III) and Cr(III) metal adsorption processes with three adsorbents including sesame stalk without pre-treatment derived from thermal decomposition of biomass, and activated carbon obtained from chemical activation of biomass in batch experiments. El Bastamy et al [21] studied the efficiency of natural Clay mineral adsorbent filtration systems in wastewater treatment for potential irrigation purposes.

Jamil, et al [22] published, application of zeolite prepared from Egyptian kaolin for removal of heavy metals. Chaves et al [23] preformed his experiment to remove the cadmium and copper by adsorption on bentonite: effects of pH and particle size. Mnasrighnimi et al [3] applied Clay Science Removal of heavy metals from aqueous solutions by adsorption using single and mixed pillared clays, Einschlag et al [9] studied wastewater treatment technologies and recent analytical developments used to purify water in the chemical industry. Mohanty et al [24] has worked on, preparation and characterization of activated carbons from *Sterculia alata* nutshell by chemical activation with zinc chloride to remove phenol from wastewater. Isaac et al [25] has studied, removal of lead and cadmium ions from water using *Annona squamosa* shell: kinetic and equilibrium studies. El-maghrabi et al [7] performed his experiment on removal of heavy metals via adsorption using natural clay material. Clay's porous nature and large surface area are advantageous for liquid absorption and heavy metal adsorption. The term "clay" refers to a naturally occurring material composed mostly of fine-grained particles (clay minerals) [26]. Nayak & Singh, stated the clay can be classified by the differences in the layered structure include smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite, and sepiolite, among others. The adsorption properties of clay minerals are due to a net negative charge on their structure. Clay's negative charge allows it to absorb positively charged species. Their huge surface area and porosity contribute to their sorption properties, Montmorillonite clay has the most surface area and cation exchange capacity of all the clays [27]. There is another classification mentioned by Macias-Quiroga et, al. based on the number and arrangement of tetrahedral and octahedral sheets in their basic structure, clay minerals are divided into three layer types (1:1, 2:1, and 2:1:1). These are further divided into five classes according to their net charge (kaolinite, mica, smectite, vermiculite, and chlorite). Smectite refers to a collection of phyllosilicate minerals that includes

montmorillonite, hectorite, saponite, beidellite, and nontronite[26]. The composition of Kaolinite clay mineral is $\text{Si}_4\text{IVAl}_4\text{VIO}_{10}(\text{OH})_8$, the symbols 'iv' represent tetrahedrally coordinated ions, while 'vi' represent octahedrally coordinated ions. where silicon occupies all tetrahedral sites and aluminum fills two-thirds of the octahedral sites (the other third of the sites being vacant)[28]. Montmorillonite has the formula $(\text{S}7.8 \text{ Al } 0.2)\text{IV}(\text{Al}3.4 \text{ Mg}0.6)\text{VIO}_{20}(\text{OH})_4$, and its theoretical composition without the interlayer material is SiO_2 , 66.7 percent, Al_2O_3 , 28.3%, and H_2O , 5%. Montmorillonite is made up of two silica tetrahedral sheets with an alumina octahedral sheet in the middle[16]. Clays play an important role in the environment by acting as a natural pollutant scavenger by removing cations and anions via ion exchange, adsorption, or both [16,29]. As a result, clays invariably contain exchangeable cations and anions that are bound to the surface. Ca^{2+} , H^+ , Mg^{2+} , K^+ , Na^+ , NH_4^+ , SO_4^{2-} , PO_4^{3-} , Cl^- and NO_3^- are the most common cations and anions found on clay surfaces. These ions can easily exchange with other ions without affecting the mineral structure of the clay [16]. Acid activation is the process of treating clay minerals with inorganic acids at high concentrations and at high temperatures. Clay mineral acid treatments are a key control over mineral weathering and genesis. exchangeable cations are frequently replaced by H^+ ions, and Al^{3+} and other cations escape from both tetrahedral and octahedral positions, leaving SiO_4 groups mostly intact, the surface area and acidity of the clay minerals are both increased as a result of this process [16,29], as well as the removal of a number of mineral impurities and the partial dissolving of the exterior layers. The overall chemical composition, the kind of cations between the layers, the type of acid, the process temperature and period, and other environmental parameters all influence the change in surface area and porous structure of clays as a result of acid treatment [16]. There are many factors that affect the adsorption process including the nature of the adsorbent and the type of treatment, the size of the pores and the surface area of the adsorbent material [30-31], effect of initial concentration [32-33], adsorbent dosage [25], contact time [7], the temperature [31], and the pH of the aqueous solution [3,31]. The purpose of this work is to prepare efficient and low-cost adsorbent (montmorillonite clay) involving activation by two activation agents H_2SO_4 and H_3PO_4 . Studied the adsorption of Cd^{2+} and Pb^{2+} in aqueous solution by the clay and compare the removal efficiency by different montmorillonite clay samples, determined the optimal adsorption conditions for the clay to remove Cd^{2+} and Pb^{2+} and its efficiency, discussed the kinetic, and thermodynamic parameters.

2. Materials and Equipment's

2.1. Materials

The chemicals used in this study: 98% extra pure Sulfuric Acid (H_2SO_4), Lead Nitrate ($\text{Pb}(\text{NO}_3)_2$), Cadmium Chloride (CdCl_2), 37% Hydrochloric Acid (HCl), 98% extra pure Sodium Hydroxide pellets (NaOH) and Phosphoric Acid (H_3PO_4). Three different clay samples which are used for this research clay1, 2 and 3, clay1 and 2 were obtained from Thi Ain village and Nawar Urban respectively and all belong Al-Baha governance, while clay 3 was obtained from Turabah Valley belonging to the Taif city.

2.2. Equipment's

pH meter Mi 105 pH/ temperature meter Milwaukee, hot plate Fisher Scientific Isotemp, Sensitive balance SHIMADSU AUW220, Oven Json-050, water distiller Gesellschaft für Labortechnik mbH D-30938 BURGWEDEL Type (2004), ICPE-9000 SHIMADZU Plasma Atomic Emission spectrometer with ASC-6100 AUTO SAMPLER SHIMADSU, Simultaneous Thermogravimetry – Differential Scanning Calorimetry (STA/TG-DSC) STA 449 F5 Jupiter – NETZSCH, XRF Rigaku WD XRF ZSX PRIMUS II, (shimadzu) GC-MS, Thermo Scientific Nicolet is50 FT-IR spectrophotometer and centurion Scientific Ltd centrifuge.

3. Methodology

3.1. Preparation and characterization of clay

It was first washed with distilled water several times in order to remove unwanted materials and water-soluble impurities. The clay was then oven-dried at 100°C for 24 h before being treated to evaporate the entire moisture content. Later on, it was used as an adsorbent. Chemical activation of the clay was done with H_2SO_4 or H_3PO_4 . 10 g of dried clay was refluxed with 100 mL (2.5 M) Acid solution. The refluxing was performed at 80°C for 3 h. After 3h, the clay was filtered then washed twice with hot water to remove residual organic and mineral matters, then dried at 80°C for 48 h. The structure of the clays as powder form was characterized before and after treatment by XRD

using Ultima IV X-ray Diffractometer in the 2θ by using Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) to determine the crystal phase of clays. The elemental configurations of the clays were analysed by XRF using Rigaku WD XRF ZSX PRIMUS II Spectrometer. TGA of the various types of clays before and after treatment was carried out with the aid of STA 449 F5 Jupiter – NETZSCH Analysis system, each powder sample was exposed constant heating rate of $20^\circ\text{C}/\text{min}$ was applied from 20 to 1000°C under nitrogen atmosphere. The vibrational behavior of the respective samples was examined by FTIR spectrometer in the range $400\text{--}4000 \text{ cm}^{-1}$.

3.2. Preparation of heavy metal solutions (stock solution)

Stock solutions of 50 ppm of Pb^{2+} and Cd^{2+} were prepared by dissolving 0.0792 and 0.0895 g of $\text{Pb}(\text{NO}_3)_2$ and CdCl_2 respectively in 1000 mL of distilled water.

3.3. Adsorption experiments

20 mL of stock solution adds to flask and the amount of adsorbent (clay) then stirred the solution for many hours, then the clay was separated from solution by centrifuge. Finally, the solutions were analyzed by ICP for determining the concentration of heavy metals. The capacity of adsorption (q_e , mg/g) onto the adsorbent at each time and removal efficiency (%) of it was calculated through the equations 1 and 2 [34-35].

$$\% \text{Removal} = \frac{(C_0 - C_f)}{C_0} * 100$$

Equation 1

C_0 is initial concentrations (mg/L). C_f is final concentrations of adsorbate (mg/L).

$$q_e = (C_0 - C_f) \frac{V}{M}$$

Equation 2

q_e is adsorption capacity (mg/g). M is mass of the adsorbent (g). V is volume of the solution (L). C_f is final concentrations of adsorbate (mg/L) [25].

Effect of parameters like adsorbent nature, adsorbent treatment, adsorbent dosage, contact time, pH and temperature was studied.

4. RESULTS AND DISCUSSIONS

4.1. Characterization of the adsorbents

4.1.1. XRF characterization

Table 1. shown the chemical compositions of adsorbents. It was determined by XRF. Table 1 summarized the chemical compositions of the clay. The constituents of the clay were SiO_2 , Al_2O_3 , and Fe_2O_3 , with additional oxides present in small amounts. Orumwense, stated that any of the major oxides present in the adsorbent, or their combined impact, is responsible for the adsorption process[40]. Table 1. showed that the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 2.48 and 5.55 for clay 2 before and after treatment respectively, this increase in value suggests increasing the presence of a large amount of free silica (Quartz). The loss on ignition was 8.01, 4.9% for Clay 2-untreated, Clay 2+ H_2SO_4 , respectively may be due to the dehydroxylation of the clay and removal of its organic and carbonate compounds[41-42]. Macias-Quiroga et, al. stated that to identify the types of clay minerals, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio has been established as a criterion, for the 40 montmorillonite samples tested, the average $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was 2.85[43]. This ratio is very close to the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of clay before treatment, indicating that the clay used in this study is montmorillonite clay.

The chemical compositions of the clay changed after the acid treatment. it shows that the percentage of SiO_2 increased whereas Al_2O_3 , Fe_2O_3 and MgO decreased for the treatment clay regarding the bulk clay[44-46] were stated that due to the exchangeable cations are replaced by H^+ ions, and Al^{3+} and other cations escape from both tetrahedral and octahedral positions, leaving SiO_4 groups mostly intact, the surface area and acidity of the clay minerals are both increased as a result of this process. Also Amari et, al. stated that the chemical examination of raw clay revealed the presence of key elements such as silica, alumina, iron, and calcium, as well as traces of sodium, potassium, phosphate, and titanium oxides, clay mineral is an aluminosilicate substance, as evidenced by the greater mass percentages of silica and alumina, clay's SiO_2 content rose after acid activation, the amount of Al_2O_3 , Fe_2O_3 , and MgO , on the other hand, has reduced, due to owing to the partial destruction (dissolution) of the octahedral layer (Al , Fe , Mg-O layers) and the exposure of the tetrahedral layers (Si-O layers) to the acid solution [47].

Table 1: Chemical compositions of the clay 2 before and after treatment by H_2SO_4

Parameter	Clay 2-	Clay 2+H2SO4
	Mass%	
Loss on Ignition LOI	8.01	4.9
Silica SiO2	39.56	57.87
Ferric Oxide Fe2O3	21.25	10.74
Aluminum Oxide Al2O3	15.97	10.43
Sulfur trioxide SO3	0.128	0.196
Chloride Cl-	0.049	0.063
Total Calcium Oxide CaO	7.823	6.542
Magnesium Oxide MgO	2.225	0.798
Sodium Oxide Na2O	1.169	1.490
Potassium Oxide K2O	1.419	2.858
Phosphorus Pentoxide P2O5	0.372	0.224
Manganese Oxide MnO	0.375	0.178
Nickel Oxide NiO	0.061	0.031
Chromium Oxide Cr2O3	0.068	0.126
Titanium Oxide TiO2	1.270	2.40
Zinc Oxide ZnO	0.141	0.274
Strontium Oxide SrO	0.144	0.175

*Ignition Loss (I.L) is measured by burning a one-gram sample at 1000°C until it reaches a constant weight [7].

4.1.2. XRD characterization

Figure 1 show XRD pattern for the adsorbents. The sharp and strong peak confirmed that the clay samples were well crystallized[50]. All XRD patterns for activation clays reflect the high existence of SiO2 peaks.

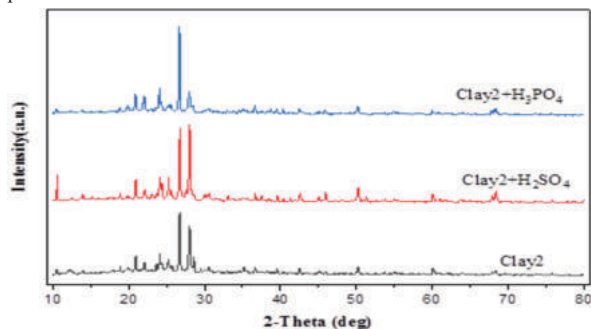


Figure 1: XRD pattern for clay 2

4.1.3. FTIR characterization

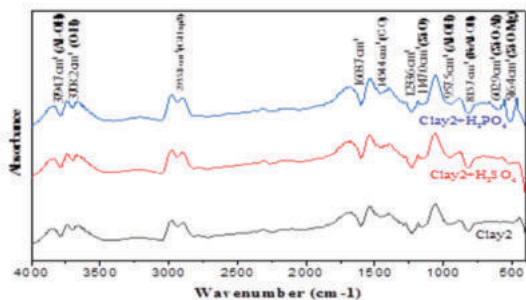


Figure 2: FTIR spectrum of clay 2

Figure 2 show the FT-IR spectrum of the clay 2. The presence of Al-OH as stretching bands at 3794.7 cm⁻¹ and as bending bands at 957.5cm⁻¹. Stretching bands at 3708.2 cm⁻¹ corresponding to the stretching vibrations of the internal O-H groups of water molecule [41]. The large band at 1233-1150 cm⁻¹ corresponds to Si-O stretching vibration, it is close to the bands that appeared in literature [43]. It shows a series of discrete peaks between 700 and 950 cm⁻¹ that indicates the cation composition in the octahedral sheet. The structural OH⁻ bending mode in montmorillonite absorbs, The OH⁻ bending mode of the Al2OH group absorbs near 957.5 cm⁻¹; The OH⁻ of Fe(III)AlOH absorbs at 815.7 cm⁻¹ [49]. The adsorption bands at 516.4 and 602.9 cm⁻¹ attributable to the deformation of Si-O-Mg and Si-O-Al, respectively[41]. The adsorption bands at 2935.8 cm⁻¹ are due to a contribution from C-H stretching that can prove the presence of C-H sp³ groups[50]. Band located at 1454 cm⁻¹ correspond to the stretching of the vibrations of C-O [42].

4.1.4. TGA characterization

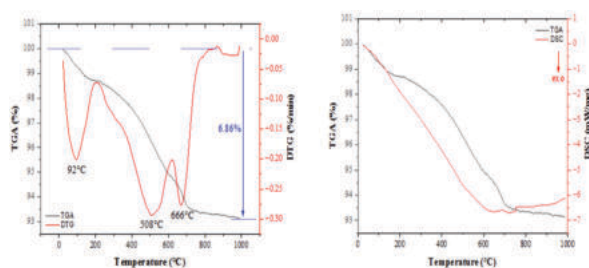


Figure 3: Thermal analysis curves for clay 2-untreated (mass change = -6.86%)

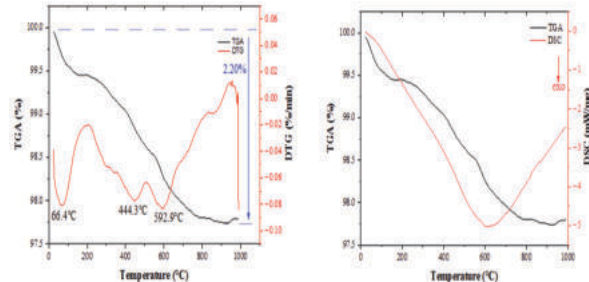


Figure 4: Thermal analysis curves for clay 2+H2SO4 (mass change = -2.20 %)

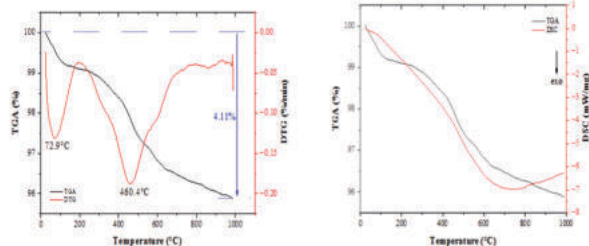


Figure 5: Thermal analysis curves for clay 2+H3PO4 (mass change = -4.11 %)

TGA analysis was carried out in order to determine how stable and potent the clay and to trace the structure changes that accompanying the thermal treatment.

The first degradation for clay 2-untreated was observed at 92°C, the second degradation was observed at 508°C, while the third degradation occurred at 666 °C as shown in Figure 3. For the clay 2 after treated with H2SO4, the first degradation at 100°C, the second degradation at 444.3°C and the third degradation occurred at 592.9°C as shown in Figure 4.

For the clay 2 after treated with H3PO4, the first degradation occurred at 72.9°C, the second degradation was observed at 460.4°C as shown in Figure 5. Clay contains water, so the first degradation for the clay 2-untreated, clay 2+H2SO4 and clay 2+H3PO4 occurred at about the same temperature as a result of a loss in the water of hydration in the formulations[51].

Percentage loss in clay 2-untreated, clay 2+H2SO4 and clay 2+H3PO4 degradation was 6.86, 2.20, and 4.11% respectively. El-maghrabi et al [7] reported that, the adsorption capacity of clay is directly proportional to the amount of water adsorbed on the clay surface, represented by the first degradation at 100-200 °C.

4.2. Removal of lead(Pb2+) and cadmium(Cd2+)

The data obtained from removal of lead ions (Pb2+) and cadmium ions (Cd2+) by modified clay, under the influence of various factors. It will be presented and discussed in comparison with other previous studies.

4.2.1. Effect of adsorbent nature and type of treatment

As shown in Fig.6, the removal of Pb2+ was 100% on clay2+H2SO4 and clay3+H3PO4. However, the clay was having an optimal condition to remove of Pb2+. As shown in Fig.7, the removal of Cd2+ was 83.19 % on clay2, which has been treated with (2.5M H2SO4). However, the clay was having an optimal condition to remove of Cd2+.

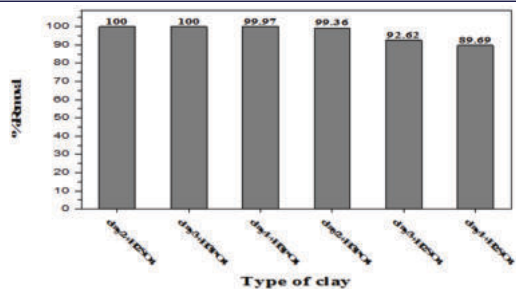


Figure 6: Effect of adsorbent nature and type of treatment on percentage removal of Pb2+ by clay (time = 5h; clay dose = 0.25g/20 mL; temp.= 25 °C; pH 5.14)

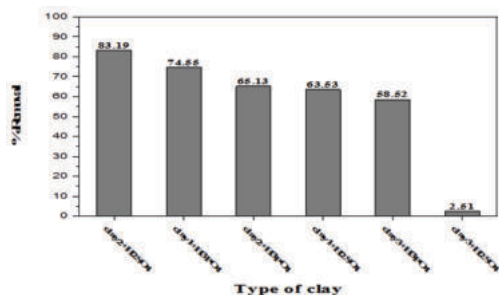


Figure 7: Effect of adsorbent nature and type of treatment on percentage removal of Cd2+ by clay (time = 5h; clay dose = 0.25g/20 mL; temp.= 25 °C; pH 5.50)

4.2.2. Effect of adsorbent dosage:

The amount of the adsorbent ranged from 0.05: 0.25 g/ 20 mL. Table 2 and Table 3 shown that, the amount of an adsorbent is directly proportional with percentage removal of lead metal. The maximum removal of Pb2+ was 100% with 0.25g of an adsorbent. The maximum removal of Cd2+ was 83.19% with 0.25g of an adsorbent. This is due to the growth into number of adsorbent sites with increasing of adsorbent dosage. Adjia et al[4] revealed the same results to remove of Pb2+ by alluvial clay. The percentage removal of Pb2+ was increased with increasing the dose of alluvial clay. El-maghrabi et al [7], stated that when the number of adsorption active sites or the surface area is increased, the availability of more exchangeable sites ensures greater absorption. Isaac et al [25], stated that the adsorption of both cadmium and lead on the surface of custard apple fruit shell (CAS) and the effect of adsorbent dosage. An amount of dosage range (10: 60mg/g) were studied, into their results observed, the maximum removal of Pb2+ was 93.08% with 0.03g as maximum amount of an adsorbent (from the initial concentration of 50mg/L) but the maximum removal of Cd2+ was 71.0% with 0.03g as maximum amount of an adsorbent (from the initial concentration of 50mg/L).

Table 2: Effect of adsorbent dosage on percentage removal of Pb2+ by clay 2+H2SO4 (time = 5h; clay dose = 0.05-0.25g/20 mL; temp.= 25°C; pH 5.14).

The weight (g)	concentration of Pb2+(ppm)	% Removal	qe(mg/g)
0.0500	0.150	99.58%	7.1500
0.1000	0.133	99.63%	7.1534
0.1500	0.564	98.43%	7.0672
0.2000	0.039	99.89%	7.1722
0.2500	0.000	100.00%	7.1800

Table 3: Effect of adsorbent dosage on percentage removal of Cd2+ by clay 2+H2SO4 (time = 5h; clay dose = 0.05-0.25g/20 mL; temp.= 25°C; pH 5.50)

The weight (g)	concentration of Cd2+ ppm)	% Removal	qe(mg/g)
0.0500	18.2	63.53%	6.34
0.1000	8.60	82.77%	8.26
0.1500	9.07	81.82%	8.166
0.2000	9.20	81.56%	8.14
0.2500	8.39	83.19%	8.302

4.2.3. Effect of time:

Table 4 and Table 5 were showed an effect of time on the adsorption process. The data was revealed that, the adsorption capacity increase with increasing of time. Removal of Pb2+ and Cd2+ increased with

time increasing. Removal of Pb2+ was 94.21% at 1h and 99.63% at 5h while, the removal of Cd2+ was 78.56% at 1h and 86.17% at 4h. Battas et al [37], explained the decrease occurs in the adsorption process by the saturation of the free adsorbent sites which may cause adsorbate release, the binding energy decreases exponentially with increasing surface saturation, according to the Freundlich hypothesis. Isaac et al [25] stated that, the concentration of Pb+2 and Cd2+ was decreased as the function of time was increased, that mean, the uptake of metal ions increased with the increase of agitation time until equilibrium was established, the adsorption process was fast in the beginning could be attributed to the increased number of active sites; however, as the process progresses becomes relatively slower, and equilibrium is attained within 30 minutes. Adjia et al [4] showed that . by using an alluvial clays for removal of lead ions by adsorption, in the range of 1-35 min, the equilibrium time needed for Pb2+ was shorter, the equilibrium is reached quickly into 30 min, indicating that the adsorption sites are well exposed. However the equilibrium time for lead adsorption. It varies according to the adsorbent material. Orumwense [40] reported that, the using of kaolinite clay to remove of lead ion from water by adsorption, the equilibrium time for Pb2+ adsorption was 2 hours. Mnasri-ghnimi et al [3], stated that the effect of time on cadmium adsorption onto pillared clay over a period of 6 hours the adsorption was rapid in the first two hours because all the available sites are empty at the beginning of the process and then gradually decreases in the third hour due to the consumed of most of the sites and also because of the repulsion that occurs between the adsorbed and free cadmium ions. Then the equilibrium occurs between the metal in the solution and the adsorption reached its maximum due to the fullness of all the available sites on the adsorbing clay.

Table 4: Effect of time on percentage removal of Pb2+ by clay 2+H2SO4 (time = 1-5h; clay dose = 0.1000 g/20 mL; temp.= 25 °C; pH 5.14).

Time (h)	concentration of Pb2+ (ppm)	% Removal	qe(mg/g)
1	2.080	94.21%	6.764
2	1.940	94.60%	6.792
3	0.158	99.56%	7.1484
4	0.128	99.64%	7.1544
5	0.133	99.63%	7.1534

Table 5: Effect of time on percentage removal of Cd2+ by clay 2+H2SO4 (time= 1-5h; clay dose = 0.1000 g/20 mL; temp.= 25 °C; pH 5.50)

Time (h)	concentration of Cd2+ (ppm)	% Removal	qe(mg/g)
1	10.7	78.56%	7.84
2	13.9	72.14%	7.2
3	19.4	61.12%	6.1
4	6.9	86.17%	8.6
5	8.6	82.77%	8.26

4.2.4. Adsorption kinetics of Pb2+ and Cd2+

Pseudo-first-order and pseudo-second-order models were applied in order to analysis of kinetic data of an adsorption of Pb2+ and Cd2+ onto clay. It is the best fitted model for the experimental data. Table 6 and Fig. 8 indicate that the regression coefficients into pseudo-second-order kinetic model of Pb2+ adsorption were almost equal as comparison to pseudo-first-order model. Table 7 and Fig. 9 indicate that the regression coefficients into pseudo-second-order kinetic model of Cd2+ adsorption were higher as comparison to pseudo-first-order model. It illustrates that, an amounts of calculated capacity (qe,cal) into pseudo-second-order model were more similar to an adsorption capacity from experiments than pseudo-first-order model (qe,exp). The adsorption behavior of Pb2+ and Cd2+ by an investigated adsorbed per time unit derives from a pseudo-second-order model [34,37, 40].

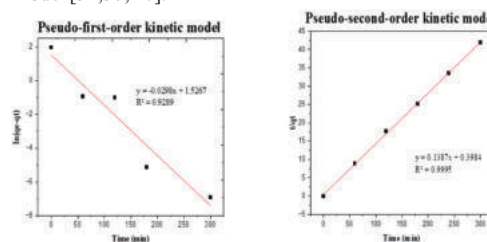


Figure 8: Pseudo-first/second-order adsorption kinetics of Pb2+ on clay 2+H2SO4

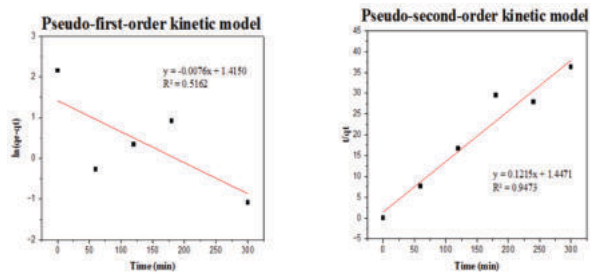


Figure 9: Pseudo-first/second-order adsorption kinetics of Cd²⁺ on (clay 2+H₂SO₄)

Table 6: Kinetic parameters for adsorption of Pb²⁺ on clay 2+H₂SO₄

Order of reaction	Parameters					
Pseudo-first-order	Intercept	slope	q _e , xp (mg/g)	q _e , cal (mg/g)	K1 (min ⁻¹)	R2
	1.5267	-0.0298	7.1544	4.602962	-0.00009933	0.9289
Pseudo-second-order	Intercept	slope		q _e , cal (mg/g)	K2 (g mg ⁻¹ min ⁻¹)	R2
	0.3984	0.1387		7.209805	0.048287	0.9995

Table 7: Kinetic parameters for adsorption of Cd²⁺ on (clay 2+H₂SO₄)

Order of reaction	Parameters					
Pseudo-first-order	Intercept	slope	q _e , xp (mg/g)	q _e , cal (mg/g)	K1 (min ⁻¹)	R2
	1.415	-0.0076	8.6	4.1165	-0.00002533	0.516
Pseudo-second-order	Intercept	slope		q _e , cal (mg/g)	K2 (g mg ⁻¹ min ⁻¹)	R2
	1.4471	0.1215		8.2305	0.010201	0.947

4.2.5. Effect of temperature

Table 8 shown that, an adsorption capacity of Pb²⁺ was increased with increasing temperature from 25: 60 °C. Table 9 shown that, an adsorption capacity of Cd²⁺ was increased with increasing temperature from 25: 60 °C. It is may be due to increase into the pores sizes by increasing the temperature. Mnasri-ghnimi et al [3] and Isaac et al [25] indicated that, an adsorption capacity of the metal ions increased by increasing temperature. It is due to increasing into an active sites by increasing temperature and that the metal ions gained enough energy to undergo interaction with the active sites, until to reach a specific temperature, further than which the desorption becomes more important, the direction occurred due to increase into the pores sizes by increasing the temperature above the ideal temperature limit. Mnasri-ghnimi et al [3] indicated that, the best adsorption temperature for cadmium, cobalt and copper ions was 45 °C by mixed pillared clays from their studying into range 30-60 °C. Isaac et al [25] studied an adsorption of four different temperatures in the range 20-50 and the initial concentration of metal ion 100 mg/L. Isaac et al [25] indicated that, an adsorption of metal ions Cd²⁺ and Pb²⁺ were endothermic adsorption that increased in adsorption value as the temperature rises. It was investigated by Gibbs free energy change, and gives it negative value.

Table 8: Effect of temperature on percentage removal of Pb²⁺ by clay 2+H₂SO₄ (time = 5h; clay dose = 0.1000 g/20 mL; temp.= 25-60 °C; pH 5.14)

Temperature (°C)	concentration of Pb ²⁺ (ppm)	%Removal	q _e (mg/g)
25	1.42	96.04%	6.8960
35	0.791	97.80%	7.0218
45	0.373	98.96%	7.1054
55	0.248	99.31%	7.1304
60	0.133	99.63%	7.1534

Table 9: Effect of temperature on percentage removal of Cd²⁺ by clay 2+H₂SO₄ (time = 5h; clay dose = 0.1000 g/20 mL; temp.= 25-60 °C; pH 5.50)

Temperature(°C)	concentration of Cd ²⁺ (ppm)	%Removal	q _e (mg/g)
25	8.60	82.77%	8.26

35	8.06	83.84%	8.17
45	7.11	85.75%	8.56
55	5.92	88.14%	8.80
60	5.34	89.29%	8.71

4.2.6. Adsorption thermodynamics of Pb²⁺ and Cd²⁺

To study of thermodynamic of the adsorption process. It should be find the following parameters ΔH°, ΔG° and ΔS°. Table 10 shown that, ΔH° values are negative and also ΔG° values for all five temperatures 25, 35, 45, 55 and 60 °C were negative. The negative amounts of ΔH° and ΔG° show that the adsorption process of Pb²⁺ on modified clay is exothermic and spontaneous. According to [34] decrease in ΔG° with rising temperature suggests that the adsorption process is undesirable at higher temperatures. The negative values of ΔS° also suggested that when the temperature in the solid/liquid phases of the adsorption process rises, the efficiency decreases. In the exothermic adsorption process -ΔH° involves either physisorption or chemisorption, or a combination of both processes [38] While its magnitude can estimate physisorption when (ΔH° ≤ 60 kJ/mol) or chemisorption (ΔH° ≥ 200 kJ/mol) [35], the values of ΔH° for Pb²⁺ on clay 2+H₂SO₄ in the range of physisorption process. Table 11 shown that, ΔH° value was positive and also ΔS° value was positive, ΔG° values were positive at low temperatures (25 and 35 °C) but negative at high temperatures (45, 55 and 60 °C) in the case of Cd²⁺. The positive values of ΔH° indicating the endothermic nature of the adsorption system and unmistakably attributable to chemisorption [36]. The negative values of ΔG° confirm the spontaneous behavior and the feasibility of the adsorption process. The positive value of ΔS° indicating the randomness and the disorderliness degree occur at the clay/cadmium interface in the adsorption process [39].

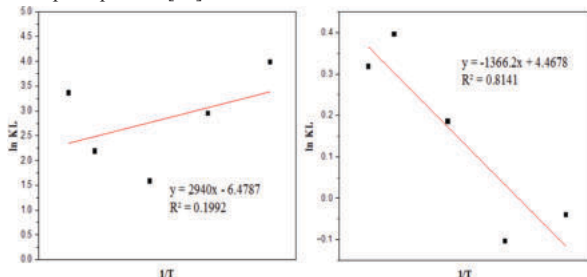


Figure 10: Vant Hoff plots of lnKL versus 1/T for adsorption of Pb²⁺ and Cd²⁺

Table 10: Thermodynamic parameters adsorption of Pb²⁺ on clay 2+H₂SO₄

Temperature (K)	lnkL	ΔG° (KJ/mol)	ΔH° KJ/mol	ΔS° J/mol	R2
298	3.9850	-9.8731	-24.4432	-53.8639	0.1992
308	2.9470	-7.5465			
318	1.5803	-4.1780			
328	2.1835	-5.9543			

Table 11: Thermodynamic parameters adsorption of Cd²⁺ on clay 2+H₂SO₄

Temperature (°K)	lnkL	ΔG° (KJ/mol)	ΔH° KJ/mol	ΔS° J/mol	R2
298	-0.0403	0.0999	11.3586	37.1453	0.8141
308	-0.1037	0.2654			
318	0.1854	-0.4901			
328	0.3960	-1.0798			

4.2.7. Effect of pH

The influence of pH on the adsorption was investigated at range of pH= 3-11 using amount of the clay (0.1000 g), an initial concentration of metals 50 ppm. Change in pH value was monitored in the case of addition the clay and before separation. Table 12 shown percentage of removal was increased as the pH increasing until arrived to pH neutral and then the adsorption decreases. Adjia et, al, and El-maghrabi et al [4, 7] stated that, the clays have a negative surface charge in solution, as the pH changes, the surface charge changes. If H⁺ ions in solution was excess, a competition between hydrogen ions H⁺ and metal ions M⁺, an available adsorption sites on the negatively charged clay surface was occurred. If pH is neutral, the positively charged of Pb²⁺ in solutions are adsorbed on the negative clay surface and thus the % removal of the metal ions reached a maximum value. On the other

hand, precipitation of metal hydroxides may also occur as the pH in solution increases, which will lead to decrease in the % removal. We concluded that, the change of pH from 3 to 7 then to 11 respectively, the best medium for adsorption of lead on the clay surface is pH neutral. Adjia et, al [4] studied that, the effect of pH on the adsorption of lead by alluvial clay in the pH range of 3-10 , revealing that , the neutral medium is better than an acid and the base .Isaac et al [25] reported that, the adsorption of both cadmium and lead on the surface of CAS, the effect of pH in the range of 2–9, the maximum adsorption at pH 5 and it was stabilized at pH 7, this was explained based on the basis of pH_{pzc} of the CAS where it competes H⁺ and metal ions, the surface of an adsorbate increase and a negative charge is able to adsorb the largest amount of metal ions . Adsorption of Cd²⁺ was examined with the pH range 3–11 and the clay amount 0.1 g and Cd²⁺ concentration 50 mg/L. Table 13 shown the amount adsorbed increased with the increase of pH due to the competition between protons and metal ions for surface sites , it reduced when increasing pH value, resulting in enhanced metal ion uptake by the adsorbent [3]. Chaves et al [23] studied that, effect of pH value into an adsorption of Cd²⁺ by the clay at pH 4-6. The results were better at pH 6. Mnasri-ghnimi et al [3] studied that, an adsorption of Cd²⁺ onto pillared bentonite at pH range 2-10, an adsorption was increased by increasing of pH value and stabilized at pH 8.8.

Table 12: Effect of pH on percentage removal of Pb²⁺ by clay 2+H₂SO₄ (time =5h; clay dose = 0.10 g/20 mL; temp.= 25 °C; pH 3-11)

pH	pH after adding clay	pH after 5 hours	concentration of Pb ²⁺ (ppm)	% Removal	qe(mg/g)
3.04	3.10	5.28	3.6900	89.72%	6.4420
5.14	-	-	0.1330	99.63%	7.1534
7.07	6.39	6.09	0.0006	100.00%	7.1799
9.06	7.17	6.74	0.1160	99.68%	7.1568
11.02	9.61	8.09	0.3200	99.11%	7.116

Table 13: Effect of pH on percentage removal of Cd²⁺ by clay 2+H₂SO₄ (time =5h; clay dose = 0.10 g/20 mL; temp.= 25 °C; pH 3-11)

pH	pH after adding clay	pH after 5 hours	concentration of Cd ²⁺ (ppm)	% Removal	qe(mg/g)
3.08	3.08	3.27	32.70	34.47%	3.44
5.50	-	-	8.60	82.77%	8.26
7.12	5.10	5.92	11.10	77.76%	7.76
9.12	8.52	6.51	6.62	86.73%	8.656
11.02	10.11	8.98	1.02	97.96%	9.776

5. CONCLUSIONS

The present study shows clay can be used as an inexpensive sorbent for the sorption of Pb²⁺ and Cd²⁺ as an inorganic pollution from aqueous solution. Adsorption of Pb²⁺, Cd²⁺ by modified montmorillonite clay were fast, with equilibrium reached in 4h for heavy metals, and they following pseudo-second-order kinetics. The maximum percentage removal of Pb²⁺ was found by clay 2+H₂SO₄ was (100%) under these parameters (time = 5h; clay dose = 0.25g/20 mL; temp.= 25 °C; pH=5.14 “pH solution without any adjustment”), and the maximum percentage removal of Cd²⁺ was found by the same clay was (97.96%) under (time = 5h; clay dose = 0.10 g/20 mL; temp.= 25 °C; pH=11). The thermodynamic parameters indicated that adsorption of Pb²⁺ on modified clay were exothermic and spontaneous. While endothermic adsorption in Cd²⁺ adsorption case which is an indication of the existence of a strong interaction between adsorbent and cadmium. The presence of a negative charge on the silica surface sites of the adsorbent is responsible for the adsorption of heavy metals. Lead removal is favored by neutral pH while the basic pH for the removal of Cadmium. The best temperature for removal of Lead and Cadmium were 25 and 55 °C respectively. From these observations, it can be concluded that modified montmorillonite clay can be used as a non-hazardous material for removal of heavy metals from contaminated water.

REFERENCES

- P. Mohajeri, C. Smith, M. R. Selamat, and H. Abdul Aziz, “Enhancing the Adsorption of Lead (II) by Bentonite Enriched with pH-Adjusted Meranti Sawdust,” *Water*, vol. 10, no. 2, 2018, doi: 10.3390/w10121875.
- L. Yan, X. Shan, B. Wen, and G. Owens, “Adsorption of cadmium onto Al 13-pillared acid-activated montmorillonite,” *J. Hazard. Mater.*, vol. 156, no. 1–3, pp. 499–508, 2008, doi: 10.1016/j.jhazmat.2007.12.045.
- S. Mnasri-ghnimi and N. Frini-srasra, “Applied Clay Science Removal of heavy metals from aqueous solutions by adsorption using single and mixed pillared clays,” *Appl. Clay Sci.*, vol. 179, p. 105151, 2019, doi: 10.1016/j.clay.2019.105151.
- H. Z. Adjia, F. Villieras, and R. Kama, “Adsorption Capacity and Mineralogical and

- Physico-Chemical Characteristics of Alluvial Clay from Far-North Cameroon,” *Int. J. Eng. Res.*, vol. 8, no. 06, pp. 1119–1129, 2019, doi: 10.17577/ijertv8i060292.
- S. M. Ghnimi and N. Frini-srasra, “A comparison of single and mixed pillared clays for zinc and chromium cations removal,” *Appl. Clay Sci.*, vol. 158, pp. 150–157, 2018, doi: 10.1016/j.clay.2018.03.019.
- R. Afroz, M. M. Masud, R. Akhtar, and J. B. Duasa, “Water Pollution: Challenges and Future Direction for Water Resource Management Policies in Malaysia,” *Environ. Urban. ASIA*, vol. 5, no. 1, pp. 63–81, 2014, doi: 10.1177/0975425314521544.
- H. H. El-maghrabi and S. Mikhail, “Removal of Heavy Metals via Adsorption using Natural Clay Material,” *J. Environ. Earth Sci.*, vol. 4, no. 19, pp. 38–47, 2014, [Online]. Available: www.iiste.org.
- N. M. Aljamali, A. M. Jawad, A. J. Alabbasy, and L. A. M. Salih, “A Literature Review on Types of Contamination (Biological, Chemical, Medical),” *Int. J. Green Chem. [IJGC]*, vol. 5, no. 1, pp. 7–14, 2019, [Online]. Available: www.journalspub.com.
- F. S. G. Einschlag and L. Carlos, *Waste Water - Treatment Technologies and Recent Analytical Developments*. InTech, 2013.
- S. Xing, M. He, T. Liu, W. Yong, and F. Zhang, “[Research progress of solid phase extraction materials in the application of metal ion pretreatment],” *Se pu = Chinese J. Chromatogr.*, vol. 39, no. 5, pp. 455–462, May 2021, doi: 10.3724/SP.J. 1123.2020.07004.
- S. M. Abdelbasir and A. E. Shalan, “An overview of nanomaterials for industrial wastewater treatment,” *Korean J. Chem. Eng.*, vol. 36, no. 8, pp. 1209–1225, 2019, doi: 10.1007/s11814-019-0306-y.
- P. S. Konostas, C. Kosma, I. Konstantinou, and T. Albanis, “Photocatalytic Treatment of Pharmaceuticals in Real Hospital Wastewaters for Effluent Quality Amelioration,” *Water*, vol. 11, no. 10, p. 2165, 2019, doi: 10.3390/w11102165.
- P. Singh et al., “Systematic review on applicability of magnetic iron oxides-integrated photocatalysts for degradation of organic pollutants in water,” *Mater. Today Chem.*, vol. 14, p. 100186, 2019, doi: 10.1016/j.mtchem.2019.08.005.
- B. A. Bhanvase, T. P. Shende, and S. H. Sonawane, “A review on graphene – TiO₂ and doped graphene – TiO₂ nanocomposite photocatalyst for water and wastewater treatment,” *Environ. Technol. Rev.*, vol. 6, no. 1, pp. 1–14, 2017, doi: 10.1080/21622515.2016.1264489.
- A. R. C. Rodriguez, “Removal of cadmium (II), lead (II) and chromium (VI) in water with nanomaterials,” *Universitat Autònoma de Barcelona*, 2015.
- K. G. Bhattacharyya and S. Sen Gupta, “Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review,” *Adv. Colloid Interface Sci.*, vol. 140, no. 2, pp. 114–131, 2008, doi: 10.1016/j.cis.2007.12.008.
- B. Abbar et al., “Experimental investigation on removal of heavy metals (Cu²⁺, Pb²⁺, and Zn²⁺) from aqueous solution by flax fibres Bouamam,” *Process Saf. Environ. Prot.*, vol. 109, pp. 639–647, 2017, doi: 10.1016/j.psep.2017.05.012.
- A. S. Thajeel, Isotherm, kinetic and thermodynamic of adsorption of heavy metal ions onto local activated carbon, *Aquat. Sci. Technol.*, 1 (2013) 53–77.
- M. Momčilović, M. Purenović, A. Bojić, A. Zarubica, M. Ran-delović, Removal of lead (II) ions from aqueous solutions by adsorption onto pine cone activated carbon, *Desalination*, 276 (2011) 53–59.
- C. Kirbıyık, A. E. Pütün, E. Pütün, Comparative studies on adsorptive removal of heavy metal ions by biosorbent, biochar and activated carbon obtained from low cost agro-residue, *Water Sci. Technol.*, 73 (2016) 423–436.
- E. E. El Bastamy, L. A. Ibrahim, A. Ghandour, M. Zelenakova, Z. Vranayova, and M. Abu-Hashim, “Efficiency of Natural Clay Mineral Adsorbent Filtration Systems in Wastewater Treatment for Potential Irrigation Purposes,” *Sustainability*, vol. 13, no. 10, p. 5738, 2021, doi: 10.3390/su13105738.
- T. S. Jamil, H. S. Ibrahim, I. H. Abd El-maksoud, and S. T. El-Wakeel, “Application of zeolite prepared from Egyptian kaolin for removal of heavy metals: I. Optimum conditions,” *Desalin. J.*, vol. 258, no. 1–3, pp. 34–40, 2010, doi: 10.1016/j.desal.2010.03.052.
- L. H. G. Chaves and G. A. Tit, “Cadmium and copper adsorption on bentonite: effects of pH and particle size,” *Rev. Ciència Agronômica*, vol. 42, no. 2, pp. 278–284, Jun. 2011, doi: 10.1590/S1806-66902011000200004.
- K. Mohanty and D. D. M. N. Biswas, “Preparation and characterization of activated carbons from *Sterculia alata* nutshell by chemical activation with zinc chloride to remove phenol from wastewater,” *Adsorption*, vol. 12, no. 2, pp. 119–132, 2006, doi: 10.1007/s10450-006-0374-2.
- C. P. J. Isaac and A. Sivakumar, “Removal of lead and cadmium ions from water using *Annona squamosa* shell: kinetic and equilibrium studies,” *Desalin. Water Treat.*, vol. 51, no. 40–42, pp. 7700–7709, 2013, doi: 10.1080/19443994.2013.778218.
- I. F. Macias-Quiroga, G. I. Giraldo-Gómez, and N. R. Sanabria-González, “Characterization of Colombian Clay and Its Potential Use as Adsorbent,” *Sci. World J.*, vol. 2018, p. 11, 2018, doi: 10.1155/2018/5969178.
- P. S. Nayak and B. K. Singh, “Instrumental characterization of clay by XRF, XRD and FTIR,” *Bull. Mater. Sci.*, vol. 30, no. 3, pp. 235–238, 2007, doi: 10.1007/s12034-007-0042-5.
- U. O. Aroke and L. A. J. Hamidu, “Instrumental Characterization of Unmodified and HDTMA-Br Modified Kaolinite Clay: SEM-EDX, Quantachrome and TGA-DTA,” *Traektorija Nauk. Path Sci.*, vol. 6, no. 6, pp. 2001–2009, 2020, doi: 10.22178/pos.59-1.
- K. G. Bhattacharyya and S. Sen Gupta, “Adsorption of Chromium (VI) from Water by Clays,” *Ind. Eng. Chem. Res.*, vol. 45, no. 21, pp. 7232–7240, 2006, doi: 10.1021/ie060586j.
- H. Al Subhi, M. S. Adee, M. Pandey, H. Al Sadeq, D. Kumar, and S. K. Shukla, “Effect of different activation agents on the pollution removal efficiency of date seed activated carbon: process optimization using response surface methodology,” *Appl. Water Sci.*, vol. 10, no. 7, pp. 1–9, 2020, doi: 10.1007/s13201-020-01251-x.
- G. M. Mafuyai, “A REVIEW OF EMPIRICAL MODELS OF SORPTION ISOTHERMS OF HYDROPHOBIC CONTAMINANTS,” *African J. environment Nat. Sci. Res.*, vol. 4, no. 3, pp. 16–44, 2021, doi: 10.52589/AJENS-02HQMMW.
- B. Abbou et al., “Removal of Cd(II), Cu(II), and Pb(II) by adsorption onto natural clay: A kinetic and thermodynamic study,” *Turkish J. Chem.*, vol. 45, no. 2, pp. 362–376, 2021, doi: 10.3906/KIM-2004-82.
- V. E. Pakade, O. B. Nchoe, L. Hlungwane, and N. T. Tavengwa, “Sequestration of hexavalent chromium from aqueous solutions by activated carbon derived from *Macadamia nutshells*,” *Water Sci. Technol.*, vol. 75, no. 1, pp. 196–206, 2017, doi: 10.2166/wst.2016.506.
- B. Kakavandi, A. Jonidi, R. Rezaei, S. Nasser, A. Ameri, and A. Esrafiy, “Synthesis and properties of Fe₃O₄-activated carbon magnetic nanoparticles for removal of aniline from aqueous solution: equilibrium, kinetic and thermodynamic studies,” *Iranian J. Environ. Health Sci. Eng.*, vol. 10, no. 1, p. 19, Dec. 2013, doi: 10.1186/1735-27461019.
- S. Ahmadi and C. A. Igwegbe, “Adsorptive removal of phenol and aniline by modified bentonite: adsorption isotherm and kinetics study,” *Appl. Water Sci.*, vol. 8, no. 6, pp. 1–8, 2018, doi: 10.1007/s13201-018-0826-3.
- H. N. Tran, S. You, and H. Chao, “Thermodynamic parameters of cadmium adsorption onto orange peel calculated from various methods: A comparison study,” *Biochem. Pharmacol.*, 2016, doi: 10.1016/j.jece.2016.05.009.
- A. Battas, A. El Gaidoumi, A. Ksakas, and A. Kherbeche, “Adsorption study for the

- removal of nitrate from water using local clay," *Sci. World J.*, vol. 2019, pp. 1–10, 2019, doi: 10.1155/2019/9529618.
38. H. Al-Johani and M. A. Salam, "Kinetics and thermodynamic study of aniline adsorption by multi-walled carbon nanotubes from aqueous solution," *J. Colloid Interface Sci.*, vol. 360, no. 2, pp. 760–767, 2011, doi: 10.1016/j.jcis.2011.04.097.
 39. G. Samudro and S. Mangkoedihardjo, "REVIEW ON BOD, COD AND BOD/COD RATIO: A TRIANGLE ZONE FOR TOXIC, BIODEGRADABLE AND STABLE LEVELS," *Int. J. Acad. Res.*, vol. 2, no. 4, pp. 235–239, 2010, [Online]. Available: www.ijar.lit.az.
 40. F. F. O. Orumwense, "Removal of lead from water by adsorption on a kaolinitic clay," *J. Chem. Technol. Biotechnol.*, vol. 65, no. 4, pp. 363–369, 1996, doi: 10.1002/(sici)1097-4660(199604)65:4<363::aid-jctb435>3.0.co;2-3.
 41. B. Abbou et al., "Removal of Cd(II), Cu(II), and Pb(II) by adsorption onto natural clay: A kinetic and thermodynamic study," *Turkish J. Chem.*, vol. 45, no. 2, pp. 362–376, 2021, doi: 10.3906/KIM-2004-82.
 42. A. Battas, A. El Gaidoumi, A. Ksakas, and A. Kherbeche, "Adsorption study for the removal of nitrate from water using local clay," *Sci. World J.*, vol. 2019, pp. 1–10, 2019, doi: 10.1155/2019/9529618.
 43. I. F. Macias-Quiroga, G. I. Giraldo-Gómez, and N. R. Sanabria-González, "Characterization of Colombian Clay and Its Potential Use as Adsorbent," *Sci. World J.*, vol. 2018, p. 11, 2018, doi: 10.1155/2018/5969178.
 44. K. G. Bhattacharyya and S. Sen Gupta, "Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review," *Adv. Colloid Interface Sci.*, vol. 140, no. 2, pp. 114–131, 2008, doi: 10.1016/j.cis.2007.12.008.
 45. K. G. Bhattacharyya and S. Sen Gupta, "Adsorption of Chromium (VI) from Water by Clays," *Ind. Eng. Chem. Res.*, vol. 45, no. 21, pp. 7232–7240, 2006, doi: 10.1021/ie060586j.
 46. G. E. Christidis, P. W. Scott, and A. C. Dunham, "Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Aegean, Greece," *Appl. Clay Sci.*, vol. 12, no. 4, pp. 329–347, 1997, doi: 10.1016/s0169-1317(97)00017-3.
 47. A. Amari, H. Gannouni, M. I. Khan, M. K. Almesfer, A. M. Elkhaleefa, and A. Gannouni, "Effect of Structure and Chemical Activation on the Adsorption Properties of Green Clay Minerals for the Removal of Cationic Dye," *Appl. Sci.*, vol. 8, no. 11, p. 2302, 2018, doi: 10.3390/app8112302.
 48. Y. Zhang et al., "Adsorption of Pb (II) and Hg (II) from aqueous solution using magnetic CoFe₂O₄ -reduced graphene oxide," *J. Mol. Liq.*, vol. 191, pp. 177–182, 2014, doi: 10.1016/j.molliq.2013.12.015.
 49. P. Djongoue and D. Njopwouo, "FT-IR Spectroscopy Applied for Surface Clays Characterization," *J. Surf. Eng. Mater. Adv. Technol.*, vol. 03, no. 04, pp. 275–282, 2013, doi: 10.4236/jsemat.2013.34037.
 50. P. Mohajeri, C. Smith, M. R. Selamat, and H. Abdul Aziz, "Enhancing the Adsorption of Lead (II) by Bentonite Enriched with pH-Adjusted Meranti Sawdust," *Water*, vol. 10, no. 2, 2018, doi: 10.3390/w10121875.
 51. B. K. Olopade et al., "Thermogravimetric analysis of modified montmorillonite clay for mycotoxin decontamination in cereal grains," *Sci. World J.*, vol. 2020, pp. 1–5, 2020, doi: 10.1155/2020/6943514.