



Physicochemical Analysis and Heavy Metals Remediation of Pharmaceutical Industry Effluent Using Bentonite Clay Modified by H₂SO₄ and HCl

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Abstract: Environmental pollution by industrial effluent has become a vital issue partly because of the detection of heavy metals in them, which need to be mitigated. Adsorbents were produced from Bentonite clay using 2 M H₂SO₄ and 2 M HCl as modifying agents in ratio 1:2 by wet impregnation method. Physicochemical properties of the pharmaceutical effluents such as pH, temperature, turbidity, conductivity, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), and heavy metals were determined. High concentrations of Fe(III) and Zn(II) were observed in the effluents when compared with standards. The optimal value of pH for Fe(III) and Zn(II) was 8, and a dose of 0.05 g was found to be the optimal value for all the adsorption system. The adsorption was best fit to Langmuir isotherm and the pseudo-second-order kinetic model. The results obtained in this study showed that the produced adsorbents could be used to supplement the commercial adsorbents in the specific application. Furthermore, the acid modification was helped to increase the sorption capacity of the clay to the heavy metals studied with H₂SO₄ being the better modification agent.

Keywords: Adsorption, Bentonite, Pharmaceutical Effluent, Heavy metals, Inorganic Acids

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INTRODUCTION

The pollution of water by industrial effluents is a serious environmental challenge in recent times due to the increased activities of industries

(such as pharmaceutical, mining, metallurgical, tannery, paint, nuclear, and batteries) (1, 2). Heavy metals can be considered as a group of trace elements with an atomic density greater than 4±1 g/cm³ (3). These include Al, Ni, As,

Co, Ag, Cr, Mn, Fe, Sn, Pb, Cd, Hg, Zn, and Cu, among others (4). Several characteristics of these heavy metals (i.e., high solubility, stability, and high migration activity in aqueous media) have led to their bio-magnification, causing varieties of human illness and other negative environmental impacts (5, 6).

A porous clay known as bentonite (with montmorillonite as its critical phase) is readily available (7, 8) and have been investigated by researchers as adsorbents to remove pesticides, herbicides (8, 9) various organic pollutants, heavy metals and a host of others (10, 11) from aqueous media. Bentonite is also very important and essential in many other fields such as iron ore pelletizing, drilling mud, foundry and binding, and civil engineering such as sealing and waterproofing (12).

Several recent modification techniques have been studied for bentonite clays in heavy metal adsorption (alongside the use of unmodified clays). Schütz *et. al* (13) modified bentonite with manganese to improve its affinity for Cd(II) uptake. Tohdee and Kaewsichan (14) utilized Bencylhexadecyldimethyl ammonium chloride for the modification of bentonite for Cu(II) and Zn(II) uptake via adsorption with positive results. Yan *et. al* (15) investigated the facile solvothermal synthesis of Fe₃O₄/bentonite for the adsorption of Pb(II), Cu(II), and Cd(II). Cantuaria *et. al* (16) studied the use of unmodified bentonite for the adsorption of silver from aqueous media. Alduaij *et. al* (17) studied the use of unmodified bentonite sourced from the Saudi area for the adsorption of Co(II).

Acid modification is a well-established preparation and modification technique for adsorbents (1). The use of inorganic acid-modified bentonite to study Zn(II) and Fe(III) sorption is unreported, leaving us a viable knowledge gap to explore. Furthermore, this study is geared towards a specific environmental problem in Nigeria, which it's Zn(II) and Fe(III) pollution from industrial effluents in Ilorin city. In this research work, the inherent adsorption strength of bentonite clays for the removal of heavy metals was investigated, and several factors (contact time, adsorbent dosage, pH, initial concentrations, and temperatures) were considered. Furthermore, isotherm, kinetics, and thermodynamics studies were conducted to gain more understanding of the adsorption process.

MATERIALS AND METHOD

Collection and Preparation of Adsorbents

The clay sample was collected from Afuze, Edo state, southern Nigeria. It was sun-dried, ground into fine powder by the use of a mortar and pestle and sieved using 2 µm geometrical sized screen. It was then transferred to a beaker and oven-dried at 110 °C for 24 h to remove water content and volatile impurities (18). The dried clay sample was removed and cooled in a desiccator containing CaCl₂ for 45-60 min. The dried clay was labeled as unmodified clay (UMBC) while the air-dried clay (size 2 µm) was equilibrated with 2.0 M sulfuric acid and stirred with a glass rod for 30 minutes and shaken for 1 h with a rotary shaker (19). The mixture was oven dried for 6 h at a temperature of 80 °C until a paste-like material is formed and allowed to cool. It was then washed several times using distilled water until the washed solution was of neutral pH. The same procedure was repeated for 2.0 M Hydrochloric acid. The two modified clays were then air-dried, sieved, and labeled as sulfuric acid modified clay (SMBC) and hydrochloric acid modified clay (HMBC), respectively (20).

Determination of Physicochemical Parameters of the Industrial Effluents

Effluent samples were analyzed to determine the pollutants/contaminants present through physicochemical analysis methods such as temperature, pH, turbidity, color and odor, and electrical conductivity.

Determination of Chemical Parameters of the Industrial Effluents

Chemical Oxygen Demand (COD)

A blank solution was prepared by pipetting a distilled water of 100 mL into a conical flask of 250 mL. A 10 mL portion of 25% H₂SO₄ and 20 mL of 0.01 M KMnO₄ was added to the solution. Then, 10 mL of the water sample was measured into another 250 mL conical flask and diluted with 90 mL of distilled water. A 10 mL portion of 25% H₂SO₄ and 20 mL of 0.01 M KMnO₄ was added to the solution. The solutions were heated on a boiling water bath for 30 minutes. Afterward, the solution in the flasks was allowed to cool, and 10 mL of 10% KI solution was added to each (21). The average values were taken by repeating the procedure three times. The chemical oxygen demand (COD) was calculated using **Eqn. 1**

$$COD = \frac{(A-B) \times M \times 40000}{\text{Volume (mL) of sample}} \quad \text{Eqn. 1}$$

Where A is the titer value of the sample, B is the titer value of the blank solution; M is the molarity of KMnO_4 and V is the volume of sample.

Dissolved Oxygen (DO)

Dissolved oxygen is the determination of the amount of oxygen present in a sample of water or wastewater at the time of collection. Winkler's titration was used for measurement (22). The average values were taken by repeating the procedure three times. **Eqn. 2** was the expression used.

$$DO \text{ (mg/L)} = \frac{1600 \times M \times V}{V_2/V_1 (V_1 - V_2)} \quad \text{Eqn. 2}$$

Biochemical Oxygen Demand (BOD)

The effluent samples were divided into two. The DO level (ppm) of the first portion was measured immediately using the method described in the dissolved oxygen test and Recorded. The second portion of the effluent sample was placed in complete darkness by wrapping the effluent sample bottles with aluminum foil at room temperature for 3 days (ASTM, 1982). The average values were taken by repeating the procedure three times.

Acidity Level

Determination of acidity level was done usually by titration. An effluent's portion of the sample was pipetted into a conical flask. Phenolphthalein indicator was added in two drops, and the solution was titrated against a standardized 0.01 M sodium hydroxide solution to a pink end-point (23). The average values were taken by repeating the procedure three times. Acidity was calculated using **Eqn. 3**

$$Acidity \text{ (mg/L)} = \frac{V \times M \times 100,000}{mL \text{ of sample used}} \quad \text{Eqn. 3}$$

Alkalinity Level

A sample of the effluent's portion was pipetted into a conical flask. Methyl red indicator was added in two drops, and the solution was titrated against a standardized 0.01M HCl solution to a pink end-point (23). The average values were taken by repeating the procedure three times. Alkalinity was calculated using **Eqn. 4**

$$Alkalinity \text{ (mg/L)} = \frac{V \times M \times 100,000}{mL \text{ of sample used}} \quad \text{Eqn. 4}$$

Total Hardness

An effluent of 25 mL was pipetted into a different conical flask. To this, 3 mL of ammonium chloride in a concentrated ammoniacal buffer ($\text{NH}_4\text{Cl}/\text{conc. NH}_3$) and Eriochrome Black T indicator was added in two drops. It was titrated against 0.01 M EDTA solution until there is a color change from violet to blue. The average values were taken by repeating the procedure three times (21). Total Hardness was calculated using **Eqn. 5**

$$Hardness \text{ in mg/L CaCO}_3 = \frac{V \times M \times 100,000}{mL \text{ of sample used}} \quad \text{Eqn. 5}$$

Heavy Metals

Iron and zinc were determined using Atomic Absorption Spectrophotometer (model AA6800-SHIMADZU) according to APHA (24).

Batch Adsorption Experiment

Effect of Initial Metal Concentration

Effect of initial metal ion concentration on percentage removal of metal ions was investigated by varying the concentration of the metal ions in the range of 5 to 50 mg/L while keeping other factors constant (i.e., time - 180 minutes, dose - 0.05 g, pH - 6, temperature - 25° C). A 50 mL portion of separate concentrations of metal ions (i.e., 20, 40, 60, 80, and 100 mg/L) was introduced into 0.05 g of clay adsorbent. The mixture was shaken vigorously and continuously on a mechanical shaker for 150 minutes and then filtered. Atomic Absorption Spectrophotometer determined the final concentration of each filtrate solution. The amount of metal ions adsorbed q_e and percentage removal of metal ions was determined.

Effect of pH

Effect of pH on percentage removal of metal ions was investigated by varying the pH from pH 2 to pH 10 with the use of 0.1 M NaOH or 0.1 M HNO_3 while keeping other factors constant (i.e., time - 180 minutes, dose - 0.05 g, temperature - 25°C, particle size - 2 μm). 0.05 g of the adsorbent was weighed into 5 beakers, and 20 mL of the industrial effluents were introduced into the beakers. The mixture was shaken vigorously and continuously on a mechanical shaker for 150 minutes and then filtered. Atomic Absorption Spectrophotometer will determine the final concentration of each filtrate solution. The amount of metal ions adsorbed q_e and percentage removal of metal ions was determined.

Effect of Contact Time

The effect of contact time on the removal of heavy metals from the industrial effluents was investigated by keeping other factors constant (i.e., dose - 0.05 g, pH - 6, temperature - 25°C, particle size - 2 µm). 1.0 g of the adsorbent was weighed into 6 beakers, and 20 mL of industrial effluents were introduced to each beaker. The mixture was shaken vigorously and continuously on a mechanical shaker for a varying period ranging from 30 - 150 minutes and then filtered. Atomic Absorption Spectrophotometer determined the final concentration of each filtrate solution. The amount of metal ions adsorbed q_e , and percentage removal of metal ions was determined.

Effect of Temperature

The effect of temperature on percentage removal of metal ions was investigated by varying the temperature of the mechanical shaker in the range of 15 to 40°C while keeping other factors constant (i.e., time - 180 minutes, pH - 6, dose - 0.05 g, particle size - 2 µm). 20 mL portions of the industrial effluent were introduced into each beaker containing 0.05 grams of the adsorbent. The mixture was shaken vigorously and continuously on a mechanical shaker for 150 minutes and then filtered at the specified temperature. Atomic Absorption Spectrophotometer determined the final concentration of each filtrate solution. The amount of the metal ions adsorbed q_e , and percentage removal of metal ions will be determined.

Effect of Adsorbent Dose

Effect of adsorbent dose on percentage removal of metal ions was investigated by varying adsorbent dose in the range of 0.05 to 2.5 g while keeping other factors constant (i.e., time - 180 minutes, pH - 6, temperature - 25 °C, particle size - 2 µm). A separate masses of the adsorbents (i.e. 0.05, 1.0, 1.5, 2.0, 2.5 g) were weighed into 5 beakers and 20 mL of the industrial effluent was introduced into each beaker. The mixture was shaken vigorously and continuously on mechanical shaker for 150 minutes and then filtered. The final concentration of filtrate solutions was then determined by atomic absorption spectrophotometer. The amount of metal ions adsorbed q_e and percentage removal of metal ions was determined.

RESULTS AND DISCUSSION**Physicochemical Parameters of Pharmaceutical Effluents**

Pharmaceutical effluents were sourced from Ilorin, Nigeria. The results of the effluent obtained were compared with the standard values of the Federal Environmental Protection Agency (FEPA) for industrial effluents, United States - Environmental Protection Agency (USEPA). National recommended water quality criteria-correction; World Health Organization (WHO).Guidelines for drinking water recommendations. **Table 1** contains the physicochemical properties of various water samples. The concentrations of heavy metals in the effluents are in the following order Fe>Zn >Cu>Mn>Pb> Cr. Nickel (Ni) and cadmium (Cd) were not detected.

Table 1: Physicochemical properties of various water samples.

Properties	Effluent	WHO ^a	FEPA ^b	USEPA
pH	6.09	6-9.5	6.0-9.0	6.0 -8.5
Temperature	33.0		40°C	
Color	Yellow	Colorless	NS	Colorless
Conductivity	451	NS	NS	NS
Turbidity	33.0	NS	NS	NS
COD	77.6	NS	NS	NS
BOD	43	NS	50	NS
TSS	71	NS	30	NS
TDS	248	<1200	2000	500
Cadmium	ND	0.003	<1	0.002
Chromium	0.001	0.05	0.015	0.05
Nickel	ND	0.02	<1	0.005
Iron	88.52	NS	20	0.3
Lead	0.002	0.01	<1	0.003
Zinc	3.276	0.01	<1	0.12
Copper	0.762	1.2	1.3	0.009
Manganese	0.701	NS	5	0.05

All values are in mg/L except conductivity (°/∞), pH, and turbidity have no unit; NS: Not stated.

Thus, the highest genotoxic risk in this study will be primarily accounted for by the higher concentrations of Fe(III) and Zn(II) in which are above the permissible level of WHO, FEPA, and USEPA.

Adsorption Parameters

Effect of Initial Concentration

Initial concentrations were considered for the adsorption studies in order to determine the equilibrium concentration of adsorbate, which was used to study other parameters. The results obtained for this study are shown in **Figure 1a**-for Fe(III) and Zn(II), respectively, and varying the initial concentrations from 20 mg/L to 100 mg/L. The notifications for the

three adsorbents are as follows; unmodified bentonite clay (UMBC), H₂SO₄ modified bentonite clay (SMBC), and HCl Modified Bentonite clay (HMBC). In **Figures 1a-b**, it was observed that the Fe(III) and Zn(II) adsorption capacity increases with increasing initial concentration and their capacities were achieved at 15.01mg/g, 8.29mg/g and 8.29mg/g for UMBC, SMBC and HMBC with Fe(III) respectively while 14.87mg/g, 7.51mg/g, and 7.98mg/g are for UMBC, SMBC and HMBC with Zn(II) respectively. The increase in adsorption capacity with initial concentration is because the concentration provides a critical mass transfer driving force for the adsorption process (25).

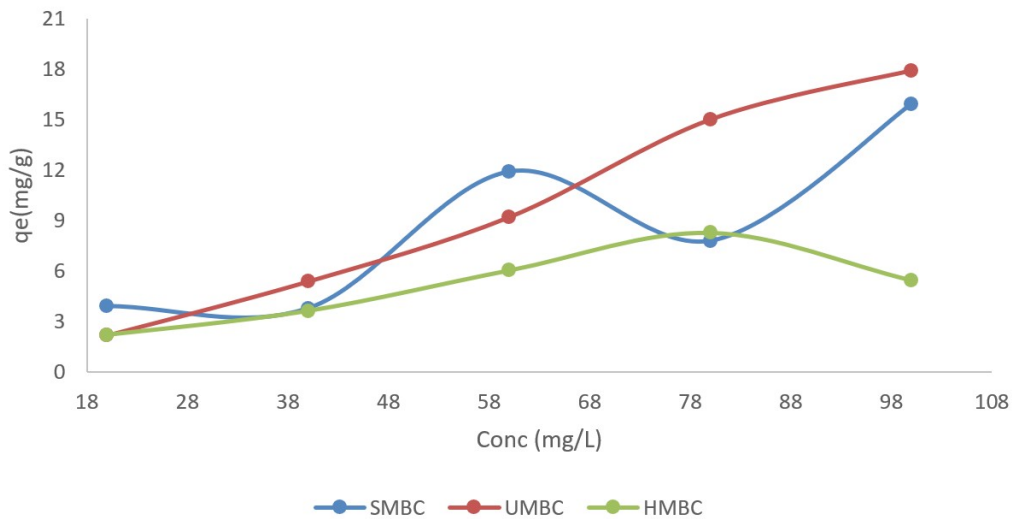


Figure 1a: Profile diagram of initial concentration on the amount of Fe(III) adsorbed using UMBC, SMBC, and HMBC.

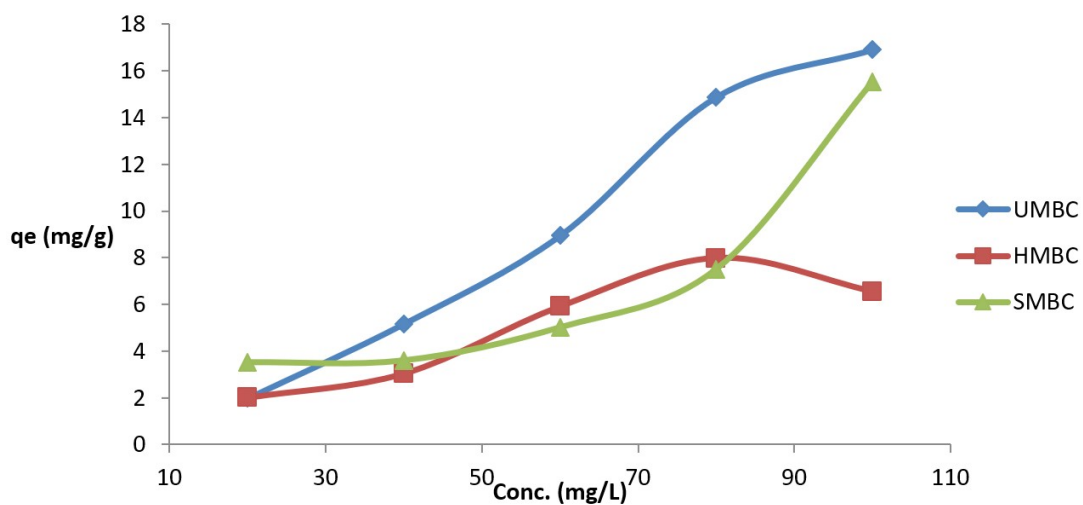


Figure 1b: Profile diagram of initial concentration on amount of Zn(II) adsorbed using UMBC, SMBC, and HMBC.

Effects of Contact Time

The pollutants' contact time with different clay adsorbents is valuable in the adsorption process due to its great deal of influence on the adsorption capacity (26). The results obtained as shown in Figures 1c-d investigate the adsorption capacity of Fe(III) and Zn(II) respectively with UMBC, SMBC, and HMBC using contact time varied from 30 min to 150 min at pH of 6, adsorbent dose of 0.05 g, the temperature of 303 K, volume of 25 mL and concentration of 88.52 mg/L and 3.26 mg/L for Fe(III) and Zn(II) respectively from the

effluent. It was noticed that as the contact time was increasing, the uptake capacity is also increased until equilibrium was achieved at 13.145 mg/g, 16.37 mg/g and 17.4624 mg/g for UMBC, SMBC and HMBC with Fe(III) respectively and 0.555 mg/g, 0.461mg/g and 0.460 mg/g for UMBC, SMBC and HMBC with Zn(II) respectively. The more significant contact times favors the adsorption process because it allows for more adsorbate molecules to overcome the mass transfer barrier (boundary layer effect) at the solid-liquid interphase.

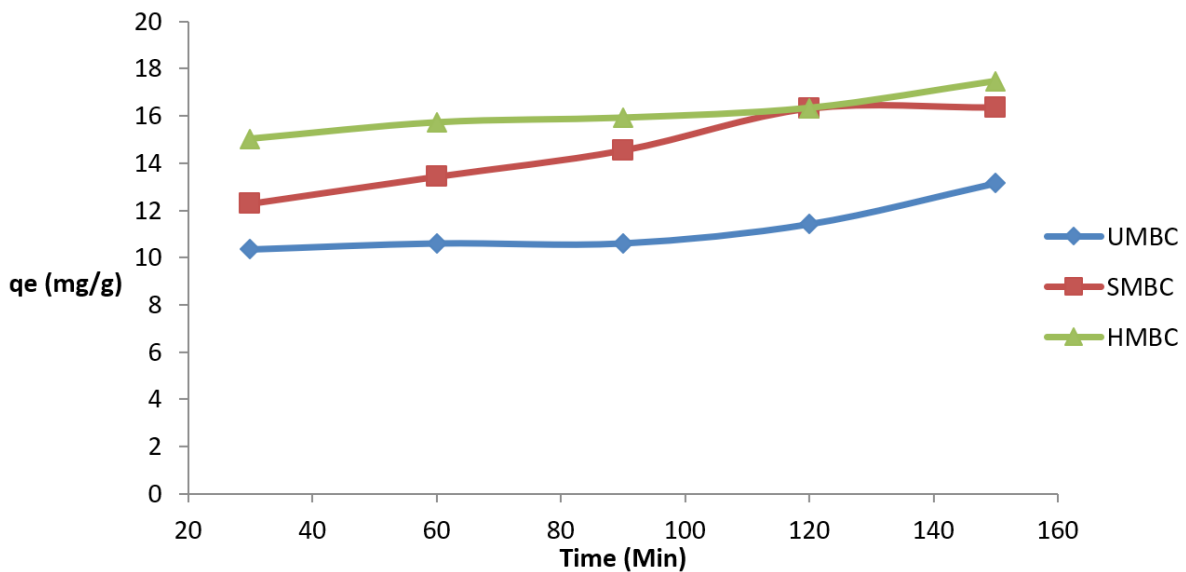


Figure 1c: Profile diagram of contact time on amount of Fe(III) adsorbed using UMBC, SMBC, and HMBC.

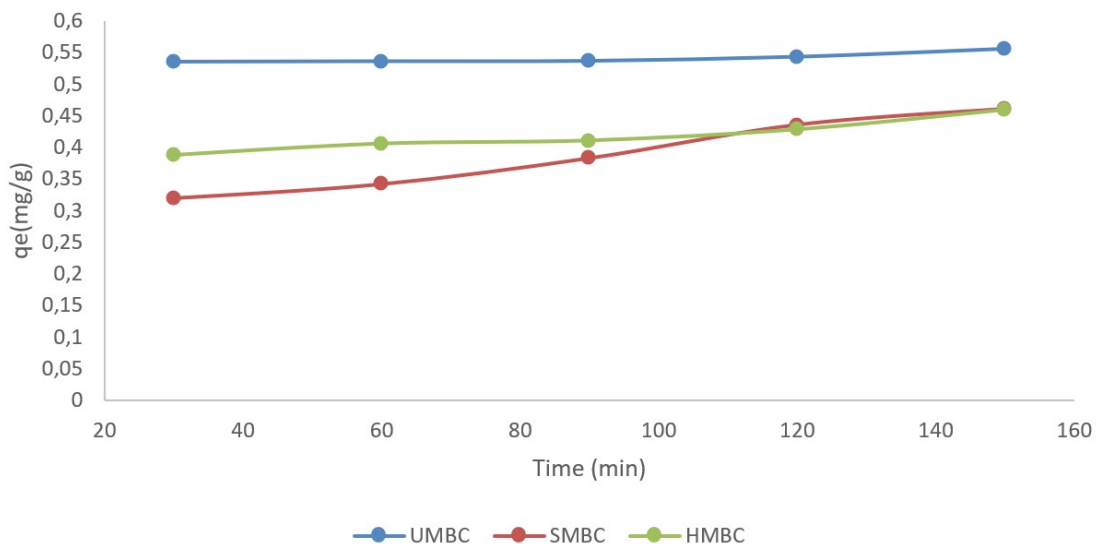


Figure 1d: Profile diagram of contact time on the amount of Zn(II) adsorbed using UMBC, SMBC, and HMBC.

Effects of Adsorbent Dose

The effect of adsorbent dose on the various adsorption systems was studied and was shown in the **Figures 1e-f** for UMBC, SMBC, and HMBC on Fe(III) and Zn(II) respectively. The parameters utilized for the adsorption process were contact time of 180 min, the volume of the adsorbate in 25 mL, pH at 6, the temperature at 303 K, and concentrations of 88.52 mg/L for Fe(III) and 3.276 mg/L for Zn(II). It was observed in **Figure 1e** that as the adsorbent dose was increased, the uptake capacity decreased and their maximum uptake was observed at 0.05 g mass of adsorbents in all the systems with the corresponding values of 24.145 mg/g, 19.78 mg/g, and 44.46 mg/g for

UMBC//Fe, SMBC//Fe, and HMBC//Fe systems respectively (27). Also in **Figure 1f**, it was observed that the adsorbent dose increase with a decrease in the uptake capacity. Maximum uptake was observed at 0.05 g mass of adsorbents in all the systems with the corresponding values of 0.933 mg/g, 0.9625 mg/g, and 3.465 mg/g for UMBC//Fe, UMKC//Zn, SMBC//Fe, SMKC//Zn, HMBC//Fe, and HMKC//Zn system respectively. The higher uptake at a more massive adsorbent dose is due to greater availability of active sites in solution onto which the adsorbate can be adsorbed.

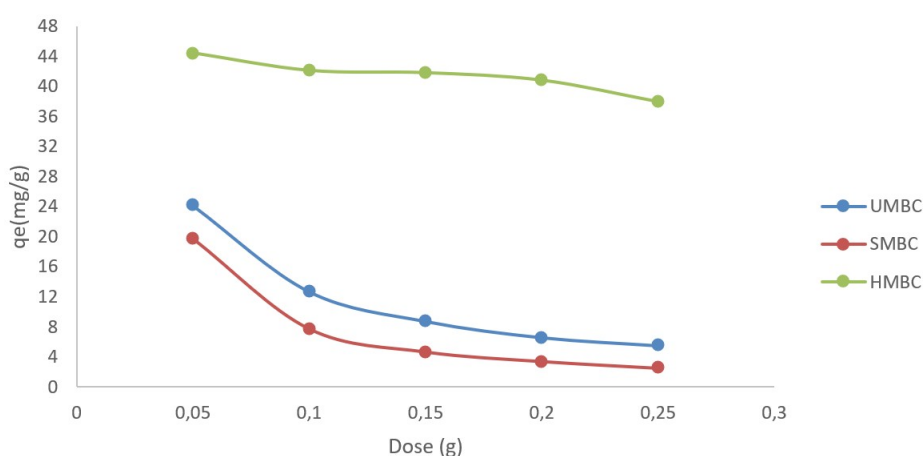


Figure 1e: Profile diagram of dose on amount of Fe(III) adsorbed using UMBC, SMBC, and HMBC.

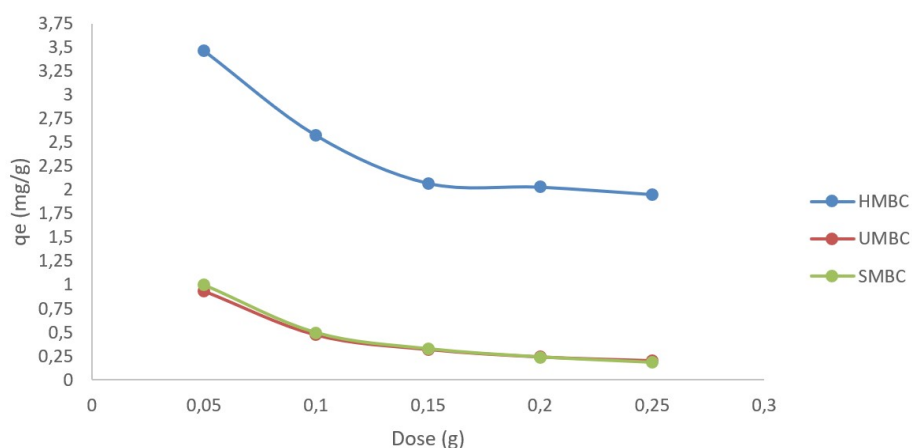


Figure 1f: Profile diagram of dose on amount of Zn(II) adsorbed using HMBC, UMBC, and SMBC.

Effect of pH

The effect of the pH is an important parameter controlling the adsorption process. It determines the influence of the adsorption capacity on the surface properties of the adsorbents and ionic forms of the metal ions in solutions (28). The pH affects the solution

chemistry of the pollutant, the activity of the functional groups in the adsorbent, and the competition of ions for binding sites (1). pH affects the charges of the adsorbate and adsorbent in solution and hence the way they interact with each other. In this study, different

pH levels ranging between 3.0 to 10.0 were considered at adsorbents dosage of 0.05 g, Temperature: 303K, and concentration of 88.52 mg/L for Fe(III) and 3.276 mg/L for Zn(II). The pH profile diagrams for UMBC, SMBC, and HMBC of Fe(III) and Zn(II) are shown in **Figures 1g-h**, respectively. In the Fe(III) system, it was noticed that uptake capacity was lowest at pH value of 3.0 with 15.935 mg/g,

11.665 mg/g, and 13.0625 mg/g for UMBC, SMBC, and HMBC respectively (19). Uptake capacity, however, increased as pH was increased from pH 3– pH 8 (UMBC//Fe, SMBC//Fe, and HMBC//Fe), and after pH 8, it starts to decrease. While in the case of Zn(II), the maximum uptake capacity was obtained at pH 7 (UMBC//Zn, SMBC//Zn, and HMBC//Zn).

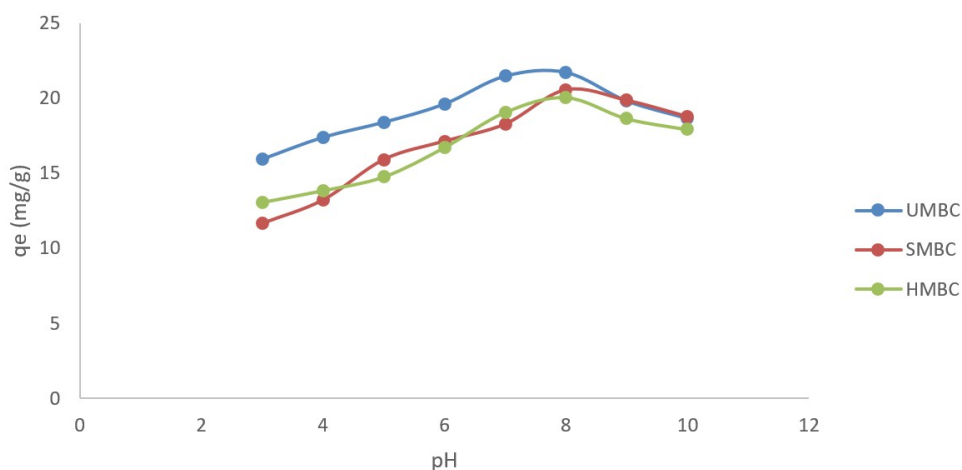


Figure 1g: Profile diagram of pH on the amount of Fe(III) adsorbed using UMBC SMBC and HMBC.

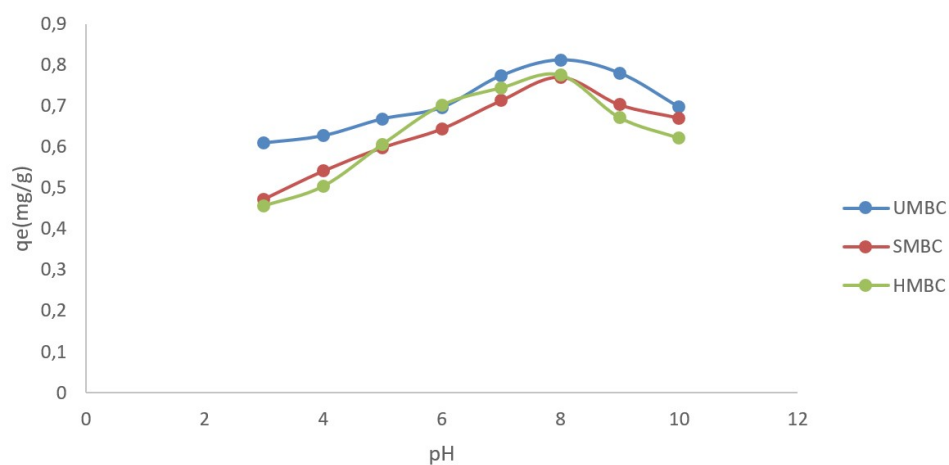


Figure 1h: Profile diagram pH on amount of Zn(II) adsorbed using UMBC, SMBC and SMBC.

Effect of Temperature

The effect of temperature on the adsorption of the Fe(III) and Zn(II) was studied using UMBC, SMBC, and HMBC. The temperature profile diagrams for the UMBC, SMBC, HMBC on Fe(III), and Zn(II) adsorption system are shown in **Figures 1i-j**, respectively. This work was studied at different temperatures ranging from 35°C to 45°C at adsorbents dosage of 0.05 g, time 180 min, 25 mL volume, the temperature is 303K, at pH 6 and concentration of 88.52 mg/L for Fe(III) and 3.276 mg/L for

Zn(II). All the sorption systems were observed to have a similar trend; as the temperature is increased, adsorbents' uptake capacity decreases. Generally, it is evidenced that the uptake capacity decreased with an increase in temperature. These observations suggest that process of adsorption in all the systems might be exothermic, and an increase in temperature could deteriorate the matrix structure of the adsorbents. The thermodynamics study confirmed this.

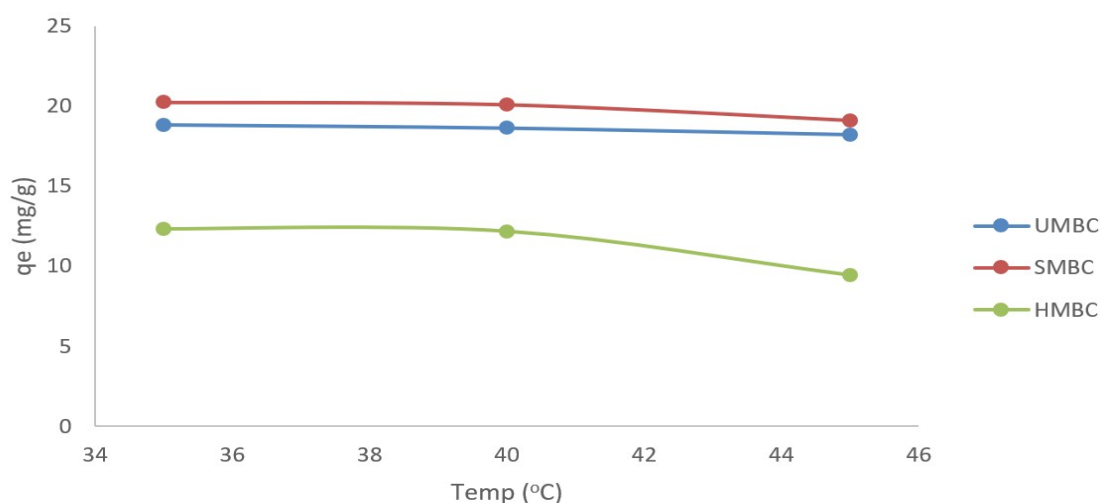


Figure 1i: Profile diagram of Temperature on the amount of Fe(III) adsorbed using HMBC, UMBC, and SMBC.

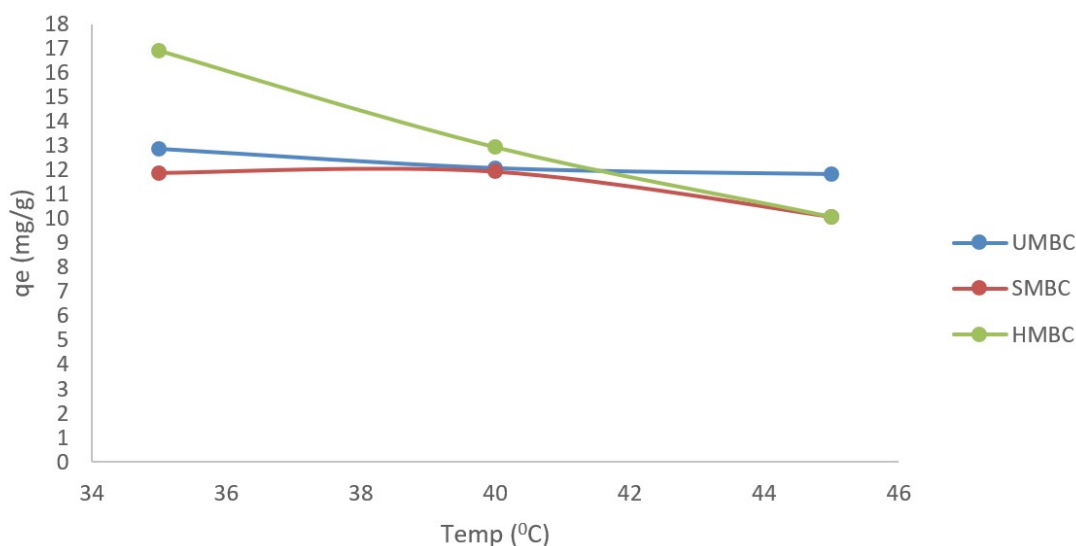


Figure 1j: Profile diagram of Temperature on amount of Zn(II) adsorbed using HMBC, UMBC, and SMBC.

Adsorption Isotherm Studies

The equilibrium adsorption data obtained in this study were fitted with two isotherms—namely, Langmuir isotherm and Freundlich isotherm, and which all explained the different degrees of success.

Langmuir Adsorption Isotherm

The data obtained from Figures 2a-b was used on this isotherm, and the parameters obtained from these plots are summarized in **Tables 2-3**. The parameters are R^2 (Correlation coefficient), Q_{\max} (maximum adsorption capacity), and R_L (dimensionless separation factor). It was noticed that the correlation coefficient for all the three systems is 0.933 for

UMBC, 0.997 for SMBC, and 0.915 for HMBC. It was noted that HMBC has an adsorption capacity value of 13.00 mg/g, which is more than that of the UMBC (4.2 mg/g) and SMBC (2.8 mg/g). Also, R_L value (dimensionless separation factor) is explained as a valuable feature in this process, and it ranges from 0 to 1 (19). As shown in **Table 2**, it affirms that the removal of heavy metals molecules is appreciated onto all the adsorbents. Furthermore, it can be observed that acid modification helped to increase the sorption capacity of the clay to the heavy metals studied.

Table 2: Langmuir adsorption parameter for various sorption systems of Fe(III).

SYSTEM (Fe)	Q_{max} (mg/g)	K_L (l/mg)	R_L	R^2
SMBC	2.8	0.09	0.009	0.987
UMBC	4.2	0.03	0.009	0.933
HMBC	13.0	0.02	0.009	0.915

Q_{max} = Maximum Adsorption capacity, K_L = Rate of Adsorption, R_L = Separation factor

Table 3: Langmuir adsorption parameter for various sorption systems of Zn(II).

SYSTEM (Zn)	Q_{max} (mg/g)	K_L (l/mg)	R_L	R^2
UMBC	2.9	0.03	0.0097	0.937
SMBC	35.5	0.02	0.0098	0.922
HMBC	14.1	0.01	0.0099	0.921

Q_{max} = Maximum Adsorption capacity, K_L = Rate of Adsorption, R_L = Separation factor

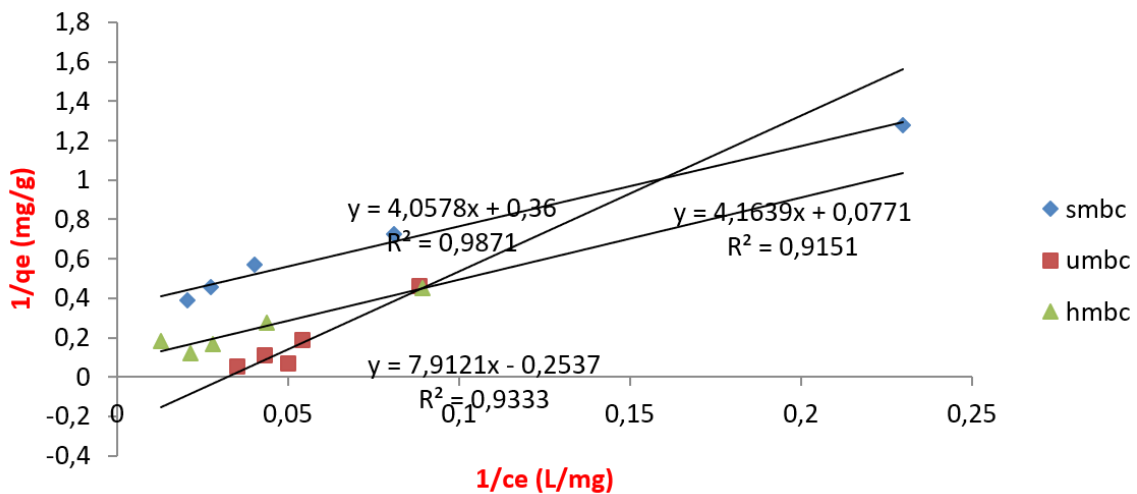


Figure 2a: Langmuir plot for UMBC//Fe, HMBC//Fe, and SMBC//Fe.

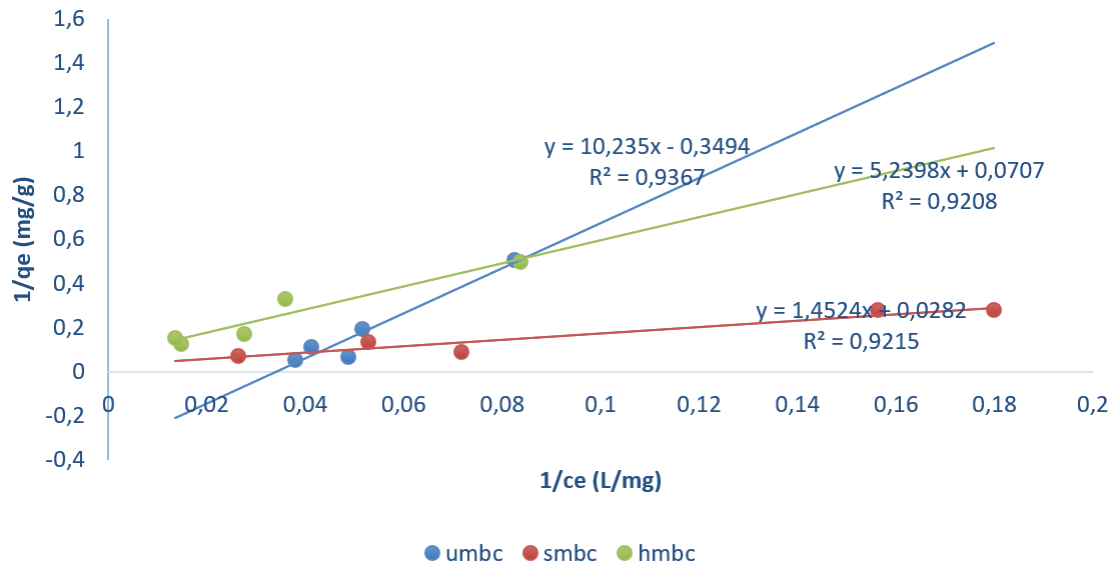


Figure 2b: Langmuir plot for UMBC//Zn, HMBC//Zn, and SMBC//Zn

Freundlich Adsorption Isotherm

The Freundlich plots for the various systems studied are given in **Figures 2c-d**, and the

parameter obtained from these plots are summarized in **Tables 4-5**. The value of $1/n < 1$ obtained in most of the adsorption system

studied indicated favorable adsorption while in the case of UMBC in which the value of $1/n$ is greater than 1 ($1/n > 1$), it indicates the unfavorable adsorption while the value of n within the range of 1 – 10 represent good adsorptions (29).

Table 4: Freundlich adsorption parameter for various adsorption systems of Fe(III)

SYSTEM (Fe)	n	1/n	K_f (mg/g)	R^2
SMBC	2.09	0.479	2.539	0.994
UMBC	0.58	1.729	13.131	0.873
HMBC	1.72	0.579	1.596	0.697

$1/n$ is the adsorption intensity and K_f is the adsorption capacity.

Table 5: Freundlich adsorption parameter for various adsorption systems of Zn(II)

SYSTEM (Zn)	n	1/n	K_f (mg/g)	R^2
UMBC	0.37	2.682	399.578	0.816
SMBC	1.34	0.746	1.023	0.860
HMBC	1.36	0.737	3.107	0.891

$1/n$ is the adsorption intensity and K_f is the adsorption capacity.

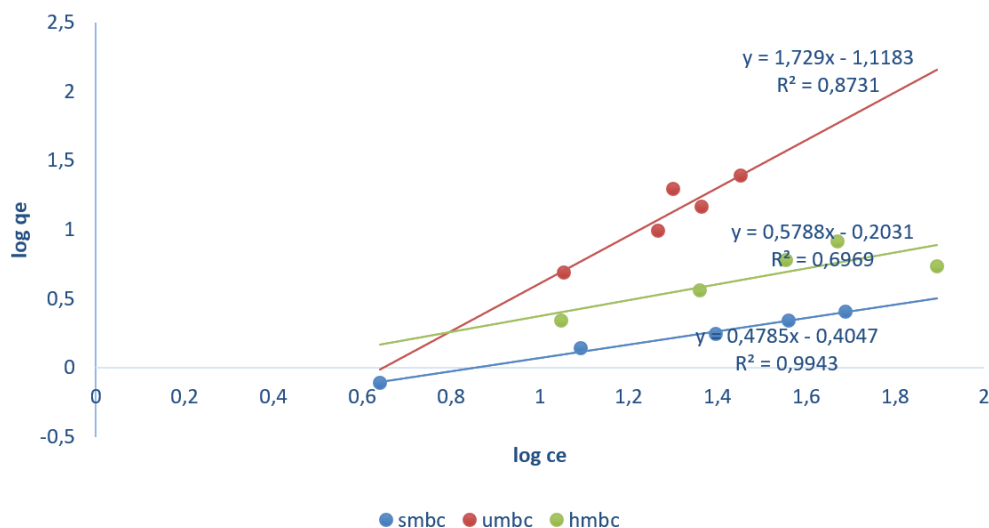


Figure 2c: Freundlich plot for UMBC//Fe, HMBC//Fe, and SMBC//Fe

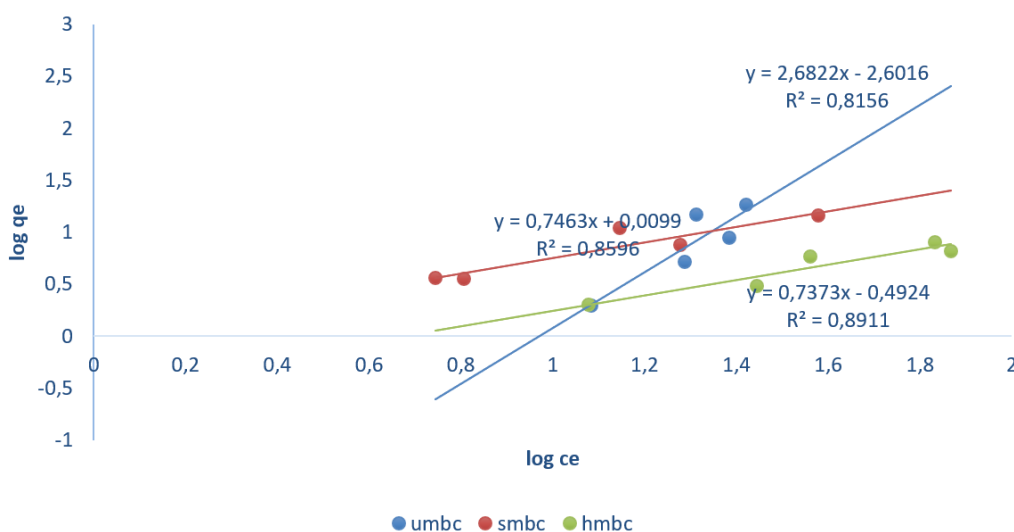


Figure 2d: Freundlich plot for UMBC//Zn, HMBC//Zn, and SMBC //Zn

Adsorption Kinetics and Mechanism

The kinetic study explains how fast the rate of adsorption occurs. Adsorption type depends on the characterization of the adsorbents and the system conditions such as contact time, concentration, and temperature. Calculation of the adsorption rate constant is fundamental to evaluate the necessary qualities of a suitable adsorbent, such as a time required for adsorbent to remove a particular compound and efficacy of the adsorbents (30). Pseudo first

order and pseudo-second-order kinetic models were employed to study the adsorption process. The validity of the kinetic models was tested by employing the correlation coefficient value (R^2). The satisfactory model had excellent linearity of the plot (high R^2 values). The pseudo-first-order plot for various adsorbents is shown in **Figures 3a-b** while the plot for pseudo-second-order for the various adsorbents is also shown in **Figures 3c-d**.

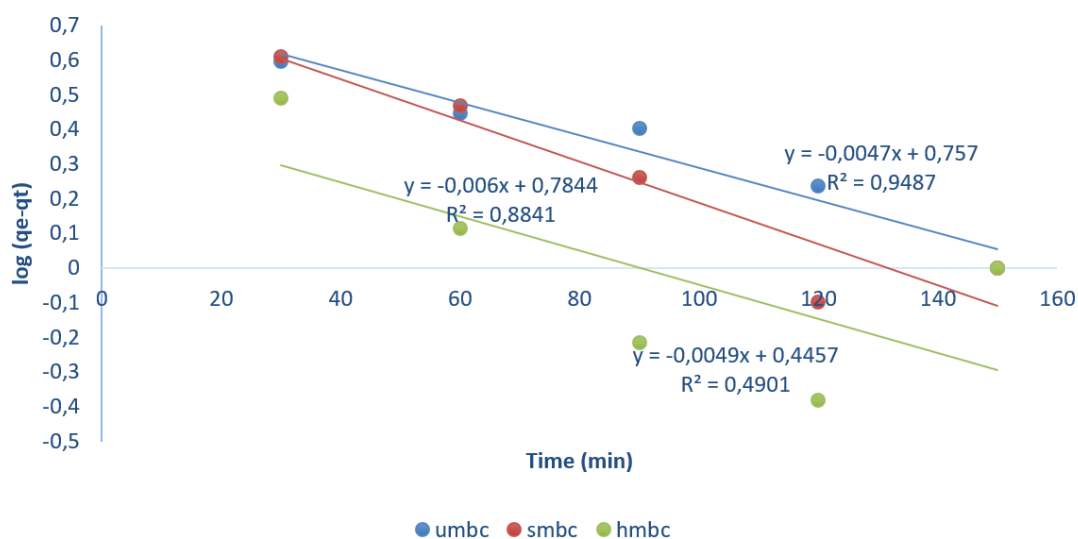


Figure 3a: Pseudo first order plot of UMBC//Fe, HMBC//Fe and SMBC//Fe.

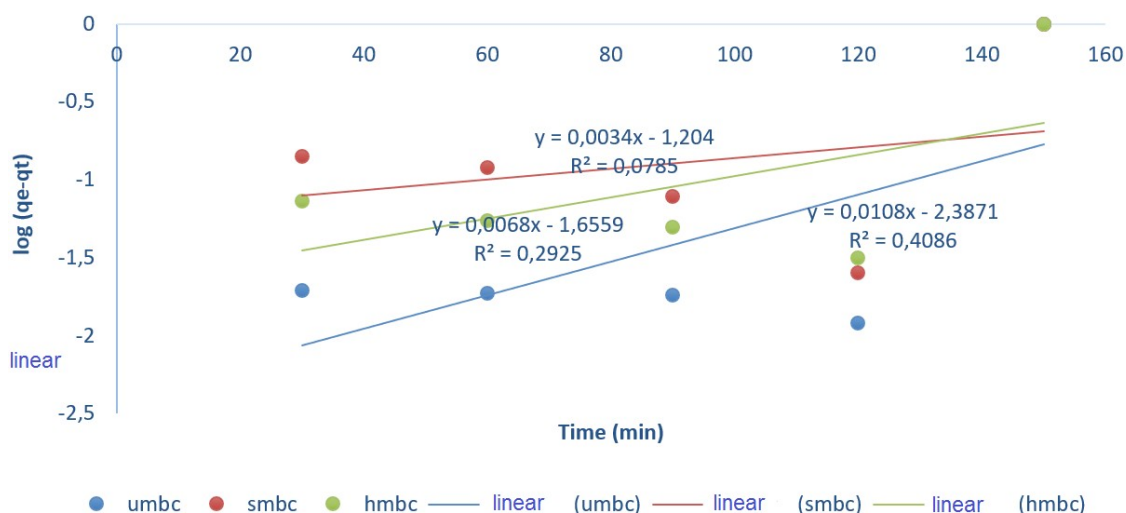


Figure 3b: Pseudo first-order plot of UMBC//Zn, HMBC//Zn, and SMBC//Zn.

The pseudo-first-order rate constant k_1 amount of Fe(III) and Zn(II) adsorbed at equilibrium q_e and correlation coefficient R^2 are shown in **Table**

6-7. Proper fitting with high R^2 was only observed for UMBC (0.948) for Fe(III), while the others showed poor agreement with kinetic

models based on their R^2 value. The parameters obtained from this model are summarised in **Table 6-7**. Therefore, the adsorption of Fe(III) and Zn(II) on different adsorbents of Bentonite

clay revealed that pseudo-first-order kinetic model failed to explain the kinetic adsorption process.

Table 6: Pseudo first order parameter for various adsorption systems of Fe(III)

SYSTEM (Fe)	k_1	q_e (mg/g)	R^2
UMBC	0.010	5.71	0.948
SMBC	0.013	6.08	0.8841
HMBC	0.011	2.79	0.4901

K_1 is the pseudo-first-order rate constant; q_e is the calculated equilibrium uptake capacities.

Table 7: Pseudo first order parameter for various adsorption systems of Zn(II)

SYSTEM (Zn)	k_1	q_e (mg/g)	R^2
UMBC	0.024	243.83	0.408
SMBC	0.007	15.99	0.078
HMBC	0.015	45.27	0.292

K_1 is pseudo-first-order rate constant; q_e is the calculated equilibrium uptake capacities.

The pseudo-second-order model showed favorable linearly with experimental data obtained for all the adsorbents. The plots are shown in **Figures 3c-d**, respectively. **Tables 8-9** tell that R^2 values of 0.972, 0.995, and 0.999 were obtained for UMBC//Fe, SMBC//Fe, and HMBC//Fe, while the R^2 values of 0.999, 0.981 and 0.993 were obtained for UMBC,

SMBC and HMBC//Zn adsorbent respectively. These are higher than corresponding R^2 values obtained in the pseudo-first-order model and described the kinetic data better. It informs that both the concentration of metal ions in solution and the number of available adsorption sites are critical in determining the rate/kinetics of the adsorption process.

Table 8: Pseudo second order parameter for various adsorption systems of Fe(III)

SYSTEM (Fe)	k_2	q_e (mg/g)	R^2
UMBC	128.53	14.29	0.972
SMBC	327.55	17.99	0.995
HMBC	563.61	17.24	0.999

K_2 is the pseudo-second-order rate constant; q_e is the calculated equilibrium uptake capacities.

Table 9: Pseudo second order parameter for various adsorption systems of Zn(II)

SYSTEM (Zn)	k_2	q_e (mg/g)	R^2
UMBC	0.076	0.56	0.999
SMBC	0.005	0.53	0.981
HMBC	0.010	0.48	0.993

K_2 is pseudo second order rate constant; q_e is the calculated equilibrium uptake capacities.

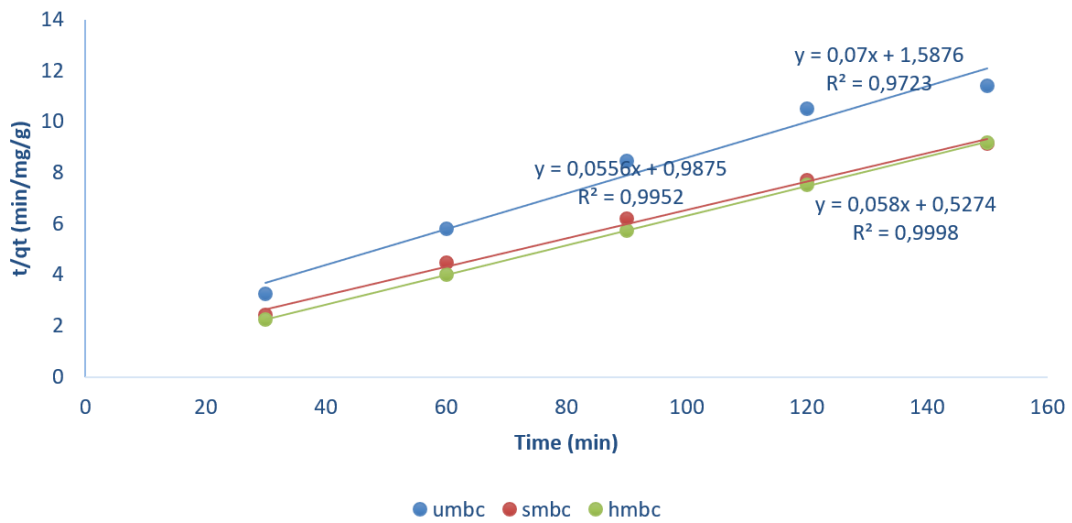


Figure 3c: Pseudo second order plot of UMBC//Fe, HMBC//Fe and SMBC//Fe.

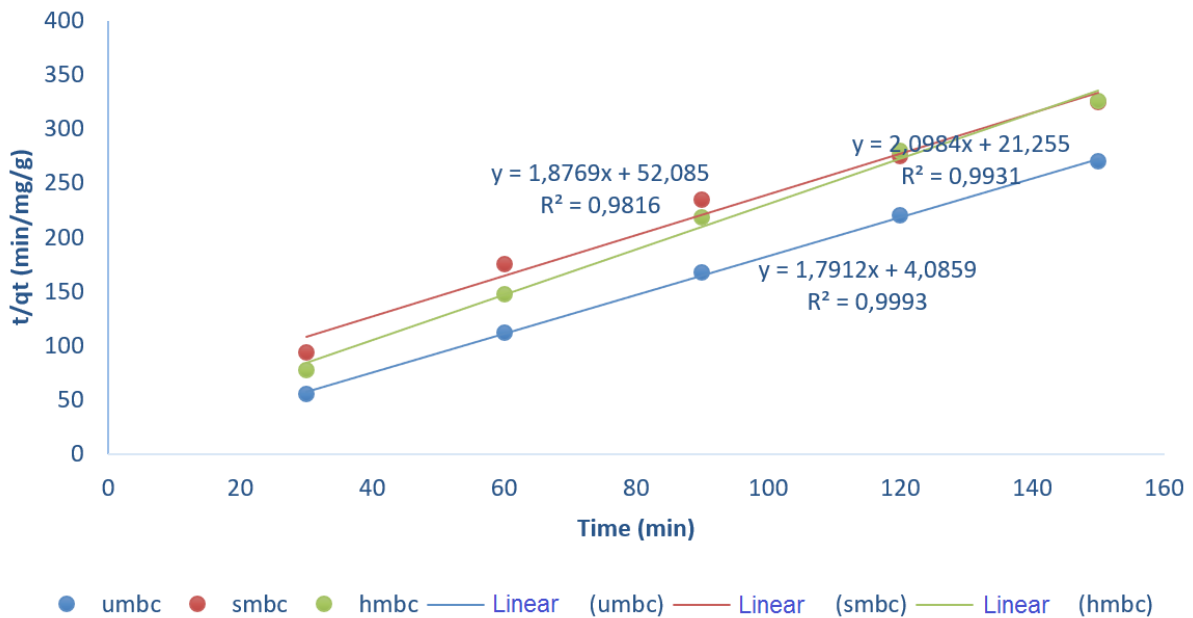


Figure 3d: Pseudo second order plot of UMBC//Zn, HMBC//Zn and SMBC//Zn

Adsorption Thermodynamics

Thermodynamic parameters can be useful in the evaluation of orientation of the adsorption process and which provide information regarding the mechanism of the process,

structural changes, and energy due to molecular adsorption ion. All the thermodynamic parameters were determined using the system of equations shown in **Eqn. 6-9**.

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{Eqn. 6,}$$

$$K = \frac{C_o - C_e}{C_o} \quad \text{Eqn. 8}$$

$$\Delta G = -RT \ln K \quad \text{Eqn. 7,}$$

$$\ln \frac{K_{s1}}{K_{s2}} = \frac{-E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad \text{Eqn. 9}$$

Where K represents the distribution coefficient, ΔH represents enthalpy, ΔS represents entropy change, and ΔG represents the free energy change of adsorption. T₁ and T₂ are the absolute temperatures, R is the gas constant, E_a is the activation energy of adsorption, K_{s1} and K_{s2} are distribution coefficient for adsorption at

temperature T₁ and T₂ respectively. The thermodynamic plot obtained from the equation for the various sorption systems studied are depicted in **Figure 4**, and the thermodynamic parameters obtained from these plots are summarised in **Table 10**.

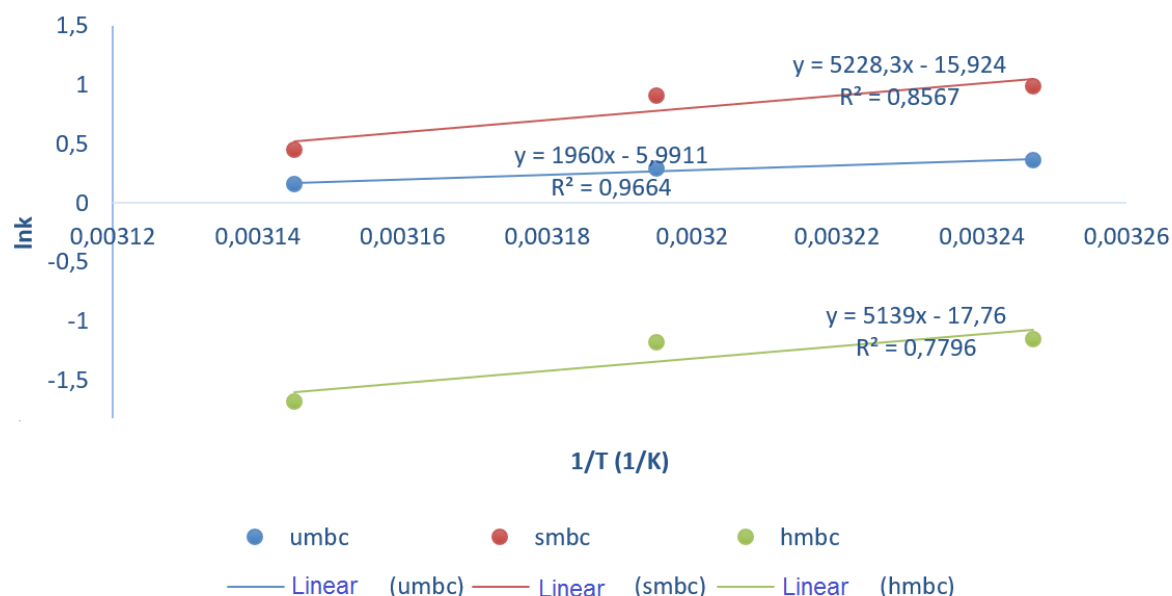


Figure 4: Thermodynamic plot of UMBC, HMBC and SMBC//Fe

Table 10: Thermodynamic parameter for various adsorption systems of Fe(III)

SYSTEM(Fe)	T (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS(J/mol/k)	R ²
Unmodified Bentonite Clay - type (UMBC//Fe)	308	-927.938	-235.61	-0.720	0.967
	313	-761.218			
	318	-428.398			
Sulphuric acid modified Bentonite Clay - type (SMBC//Fe)	308	-2536.61	-628.79	-1.914	0.858
	313	-2358.68			
	318	-1202.51			
Hydrochloric acid Modified Bentonite Clay - type (HMBC//Fe)	308	2952.444	618.21	2.136	0.781
	313	3071.783			
	318	4442.479			

The thermodynamic plot for the following adsorbents, namely, UMBC are plotted in **Figure 4** gave R² value of 0.967. The relatively high R² values can be attributed to the regular trends exhibited in their respective temperature

profile diagram except for SMBC and HMBC with 0.858 and 0.781 respectively of R² value, which exhibited irregular trends in his temperature profile diagram. From **Table 10**, it was observed that all the ΔG values in the

adsorption system are negative, which suggested that the process of adsorption is spontaneous over the range of temperature studied except for HMBC and HMKC in which ΔG values are positive which indicate that the process of adsorption is not spontaneous. The ΔS values of -0.720 J/mol/k , -1.914 J/mol/k and 2.136 J/mol/K for UMBC, SMBC, and HMBC, respectively, which indicate that there is decrease and increase in randomness at the solid/solution interface during the adsorption. The ΔH values were found to be -235.61 KJ/mol , and -628.79 KJ/mol , for UMBC, SMBC respectively suggest that the process is exothermic while ΔH values were found to be 618.21 KJ/mol for HMBC which indicate that the process is endothermic.

CONCLUSION

From this study, acid-modified adsorbents were successfully prepared from Bentonite clays. Physicochemical properties of modified and unmodified adsorbents were observed to have significant differences in all parameters. Adsorbent dosage of 0.05 g and pH values of 8 were found to be the optimal value. The adsorption data in this study were best explained using the Langmuir isotherm model. Sulfuric acid-modified bentonite clay (SMBC) performs best among all the adsorbents. The kinetic data in this study was best explained by the pseudo-second-order kinetic model implying the physisorption process. The thermodynamic data show that HMBC showed that the process is endothermic and non-spontaneous. Negative of ΔS values indicated that there is a decrease in randomness except for HMBC at the solid/solution interface during the adsorption. Furthermore, it was observed that acid modification was helped to increase the sorption capacity of the clay to the heavy metals studied.

DISCLOSURE STATEMENT

Conflict of Interest: The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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