

Equilibrium and Kinetics Study of Iron Adsorption from waste water using Chemical Modified Bentonite as efficient adsorbents

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Abstract

This study analyzed the adsorption properties of bentonite clay after chemical activation by sulfuric, hydrochloric and nitric acids. The treated samples were characterized using SEM and Fourier Transform Infrared (FTIR) Spectroscopy. The adsorptive capacities of the samples were investigated by using them to adsorb Iron from wastewater. The parameters that affect the Iron adsorption, such as contact time, solution pH, initial Iron concentration, and temperature, have been investigated and optimized conditions were determined. Equilibrium isotherm studies were used to evaluate the maximum adsorption capacity of activated Bentonite and the experimental results showed this to be sulfuric acid high capacity than hydrochloric and nitric acids (about 30, 23 and 19) mg/g respectively.

Keywords: Iron, adsorption, waste water, Equilibrium isotherm and activated Bentonite

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I. INTRODUCTION

Most of the heavy metals discharged into the wastewater are found toxic and carcinogenic and cause a serious threat to the human health. [1]. The release of large quantities of hazardous materials into the natural environment has resulted in a number of environmental problems and due to their non-biodegradability and persistence, can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health. Heavy metals can be absorbed by living organisms; however unlike organic contaminants, they are not biodegradable and tend to accumulate in living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body [2, 3]. As a trace element, some heavy metals (e.g. selenium, cobalt, copper, iron, manganese, molybdenum, vanadium, strontium and zinc) are essential to maintain the metabolism of living organisms. However, at higher concentrations they may pose a health risk to humans and to the environment and lead to poisoning [4] Non-essential heavy metals of particular concern to surface water are cadmium, chromium, mercury, lead, arsenic, and antimony [5]. Also, trace metals such as lead and cadmium interfere with essential nutrients of similar appearance, such as calcium and zinc [6, 7]. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies: electrochemical treatments, photocatalytic processes and new adsorbent/reactive media of mineral, organic or biological origin represent the new trends in the physico-chemical water treatment field for the removal of inorganic contaminated waters [2].

Electrochemical treatments include electrodialysis and ion-exchange electrodialysis, electrocoagulation, electroflotation, electrodeposition [6]. Electrodialysis offers advantages such as the ability to produce a highly concentrated stream for recovery and high separation selectivity. However, since it is a membrane process, it requires clean feed, careful operation and periodic maintenance to prevent any stack

damages thus increasing process costs. Electrocoagulation, electroflotation, electrodeposition involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state [3]. However, in addition to energy costs, another disadvantage lies in the corrosion that can become a significant limiting factor since electrodes have frequently to be replaced [8]. Heavy metal removal from effluents can be achieved by conventional treatment processes such as chemical precipitation, flotation, ion exchange, membrane separation and adsorption on activated carbon [2].

Chemical precipitation, obtained with lime and limestone by adjusting the pH to the basic conditions (pH 9-11), is the most widely used process for heavy metal removal from effluents. It can be employed to effectively treat high metal concentration of more than 1000 mg/L; other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement and convenient and safe operations. However, chemical precipitation is a long time process: shorter time to settle out suspended solids can be achieved by dosing coagulants, thus improving sludge settling. Nonetheless, large amounts of chemicals are needed and the production of excessive sludge amounts requires further treatment [9-11].

A number of natural materials (as adsorbent) were tested such as polymeric materials, and activated carbon [12-16]. Clay materials are one of the low-cost natural materials that may be used as ion exchangers for the removal of heavy metals from waters [17]. The main aim of bentonite is cost effective and simple approach to remove iron from wastewater activated bentonite ,because of its cheap ,effective and economic method with high potential for the removal iron, recovery and recycling of metal ions from aqueous solution, and easy to adapt have received much attention in heavy metals adsorption from waste water.

Chemical modifications on the clays surface with mineral acid solution, usually sulfuric or hydrochloric acids were conducted to improve the clays adsorption capacity by increasing the specific surface area (SSA), porosity and increase the overall negative charge [18].

This paper deal aims to investigate the iron adsorption from wastewater by activated Bentonite materials by batch kinetics and equilibrium studies.

2. Experimental

2.1. Materials and Reagents

H₂SO₄, HCl and HNO₃ acids were chemical reagent grade and were supplied from ADWIC, Egypt. bentonite clay was obtained from Egypt-Alexandria desert road near Wadi El-Natron by *Al Amier Ceramic Co. Cairo*. (Table 1). The provided clay samples were crushed, ground in a mortar and sieved to the used grain size of 200 mesh size. The clay samples were purified by water gravitational sedimentation. The washed solid clay sample was dried in electric furnace at 110 °C until complete dryness.

Crude waste water under study was produced from Drinking water purification plant - 10th of Ramadan City, its chemical composition is given in (Table 2).

Table 1. Chemical composition of the working bentonite sample

Constituent	%	Constituent	%
Al ₂ O ₃	16.60	MgO	2.13
SiO ₂	41.10	CaO	7.96
TiO ₂	0.98	Na ₂ O	5.46
Fe ₂ O ₃	7.41	P ₂ O ₅	0.17
MnO	0.04		

Table (2): Chemical analysis of waste water.

Component	Concentration, mg/l
Fe	150
Zn	16
Mn	270
Cu	12
Cd	0.5
Al	13

2.2. Preparation of activated Bentonite

activated Bentonite (BS, BN and BH) was conducted by adding 50 g of bentonite to 500 mL of sulfuric acid, nitric acid and hydrochloric acid solution (2M) and refluxing at 110°C under atmospheric pressure for 4

hours. The activated solid was washed with distilled water until free from undesirable metal and dried at 80 °C. The dried samples were gently crushed and packed into plastic containers for further use.

2.3. Clay samples characterization:

Fourier Transform Infrared Spectrometer (FTIR): (FTIR) model Thermo Scientific Nicolet IS10, Germany.

Scanning Electron Microscope (SEM): SEM model Philips XL 30 ESEM (25-30keV accelerating voltage, 1-2mm beam diameter and 60-120 s counting time). Minimum detectable weight concentration is ranging from 0.1 to 1 wt % with realized precision lower than 1%.

2.4. Apparatus:

The reaction was carried out in a cylindrical 250 ml reactor of 10 cm diameter. It was fitted with Teflon-coated stirrer with 2cm diameter and placed in thermostatically controlled water bath. The impeller tip speed was **adjusted** at 300 rpm. Filtration was performed using Buchner type filter of 4.6 inch. diameter. Polypropylene filter cloth of 80 mesh aperture size was used. A vacuum pump was used for filtration.

2.5. Equilibrium Studies

For studying the relevant adsorption factors, several series of experiments have been performed using the iron synthetic solution. These factors involved contact time, initial iron concentration, pH and the adsorption temperature. From the obtained results, Langmuir and Freundlich isotherms were resolved. These batch adsorption experiments were performed by shaking 0.12 g of clay sample with 15 ml of the iron synthetic solution (100 ppm) using a magnetic stirrer. The adsorbed amounts of iron were calculated by the difference between its equilibrium and initial concentrations.

For eluting or de-sorption of the loaded iron from the clay, this was then followed by studying the proper eluent solutions, namely CH₃COONa, HNO₃, HCl, and NaCl.

3. Results and discussion

3.1. Characterization of raw materials

3.1.1. FTIR Study

FTIR spectra of different chemical activated Bentonite clays are presented in (**Figure 2**). B-H₂SO₄, B-HCL and B-HNO₃, depends on its functional groups reactivity. IR spectra of H₂SO₄(1befor, 4after sorption), B-HCL(2befor, 5after sorption) and B-HNO₃(3befor, 6after sorption) complexed with Fe ions were shown in **Fig. 1** As can be seen in **Fig. 1**: by compare the FTIR bands before and after sorption, the data showed that there is an additional bands at 3400, 2350, 1340 and 464 cm⁻¹ and reaming other bands intensity were reduced 3240 cm⁻¹ at B-H₂SO₄. The band at 1186cm⁻¹ disappeared with B-HNO₃ due to the increased substitution of metal by iron ions. Whereas, the intensity of FTIR bands in case of B-HCL were decreased except the FTIR band at 1500 and appear at 1384 was vanished. These results may be confirmed that the formation of new bonds or complexation of metals with B-HCL

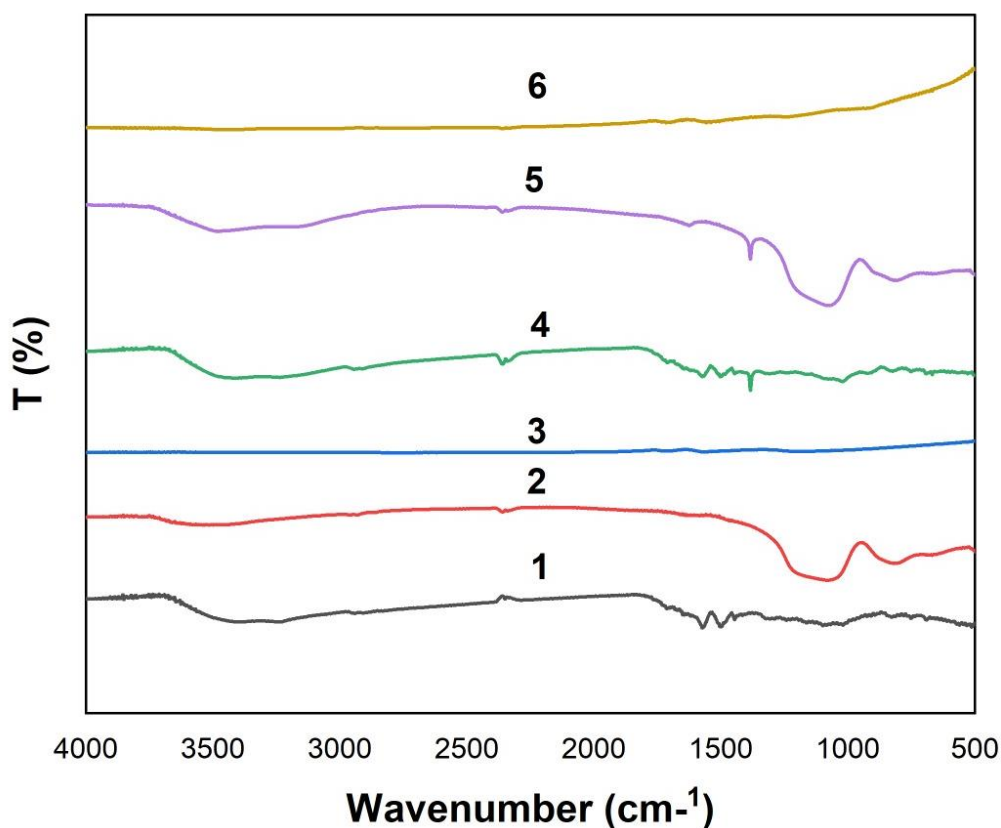


Figure (1): FTIR spectra of working clay samples before and after sorption, H_2SO_4 (1, 4), B-HCL(2, 5) and B- HNO_3 (3, 6)

3.1.2. Surface morphology studies:

SEM images of the macrostructure B- H_2SO_4 , B-HCL and B- HNO_3 before and after iron adsorption **Fig. 2** showed the rudimentary on the B- H_2SO_4 (a), B-HCL(c) and B- HNO_3 (e), surface which formed due to the volatility and constitute decomposition during chemical treatment. After adsorption, these pores and crevices were occupied with iron ions (**Fig.2 b,d,f**).

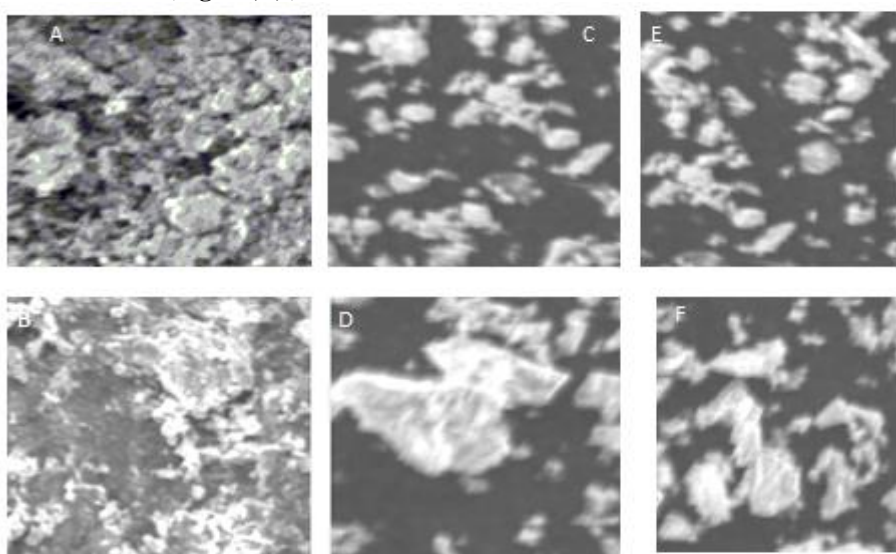
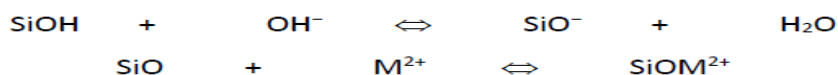


Fig. (2): SEM images of B- H_2SO_4 , B-HCL and B- HNO_3 (a,c,e) before and (b,d,f) after iron adsorption

3.2. Batch investigation

3.2.1. Effect of pH:

Effect of pH on Fe adsorption efficiency (A%) from the synthetic solution by various clay was studied in the range from 0.5 to 8 while the other parameters were kept constant at S/A phase ratio 0.12 g/ 15 ml; 100 ppm concentration for 120 min. contact time at room temperature (25±2) °C. From the obtained results shown in Figure (3), it is clearly evident that Fe adsorption efficiency (A%) increased up to (86,84 and 68) % at BS, BN and BH respectively, at pH2.8. At pH above adsorption efficiency decreased. Thus, solution with pH 2.8 would be used in the next experiments. In an alkaline medium, the surface of clay becomes negatively charged and electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal adsorption. This mechanism can be shown as follows:



A similar theory was proposed by several earlier workers for metal adsorption on different adsorbents [19].

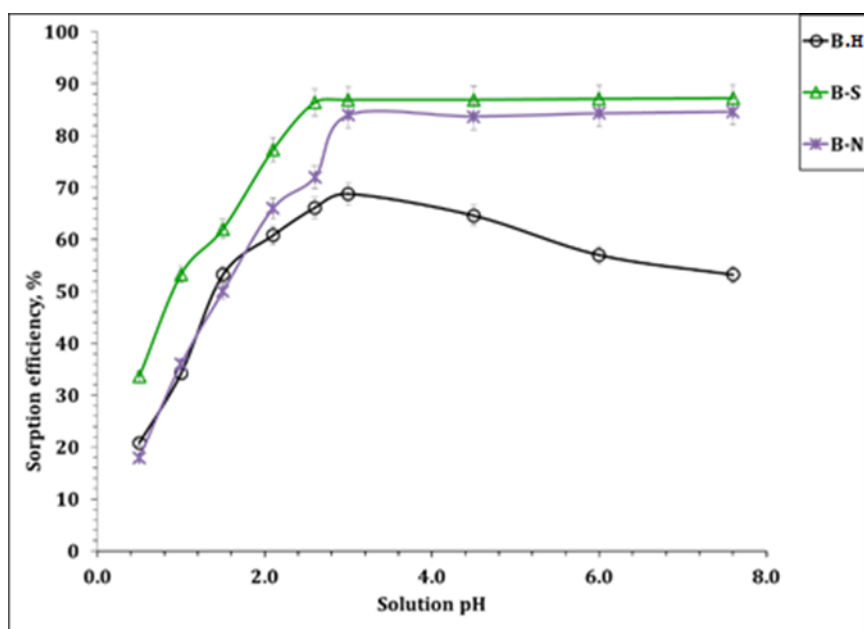


Figure (3): Effect of PH on iron adsorption efficiency, % (0.12 g/ 15 ml of wastewater; room temperature, 400 rpm).

3.2.2. Effect of the adsorption time

The adsorption time of iron by various types of bentonite (BS, BN and BH) at different times (5, 15, 30, 45, 60, 90, and 800 min) was carried out. **pH 2.8, 0.12 g/ 15 ml wastewater, 100 ppm iron** at room temperature. The experimental results are given in (Figure 4) as a relation between iron adsorption efficiency % and time. From the results, it is found that the adsorption of iron by different types of modified bentonite is improved with increasing adsorption time until a constant state at 720 min and there is simply change after that time. The increasing adsorption rate at the origination is due to availability of large number of vacant sites for adsorption of iron. Adsorption efficiency of (BS) larger than (BN) and (BH).

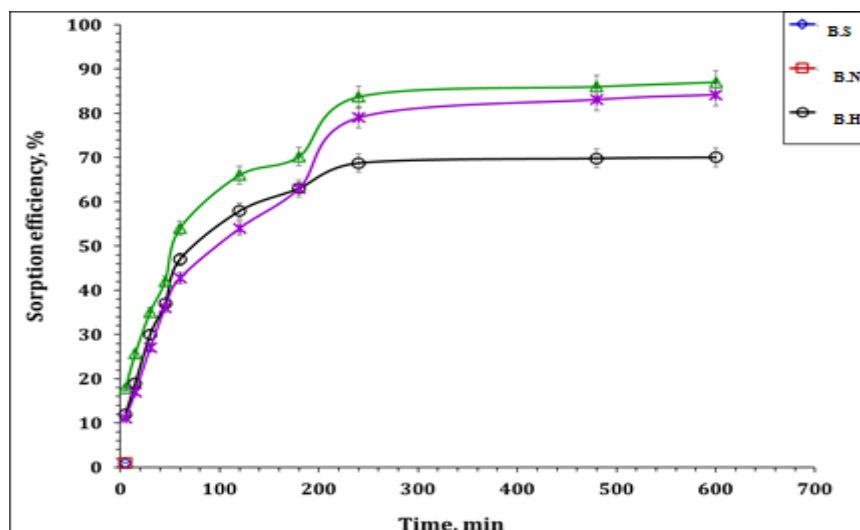


Figure (4): Effect of adsorption time on iron adsorption efficiency, % (0.12 g/ 15 ml of wastewater; room temperature, 400 rpm).

3.2.3. Effect of the amount of adsorbents

We followed the evolution of the removal efficiency of iron (2 - 12 g/L). Other parameters were reserved unchanging at temperature of about 20 °C, Measuring the iron content of the treated samples was made after 720 minutes contact with the activated Bentonite clays. The obtained data are given in (Figure 5) as a relation between iron adsorption efficiency % and clay amount of addition.

The results shown in (Figure 5) clear that the iron removal efficiency raised with increasing dose of bentonite clays introduced. Note that for amount of clay (8 g/L), the best yields 90, 85 and 75% for (BS) , (BN) and (BH)., respectively. But the amount of iron q_e mg/g decrease with increasing amount of addition.

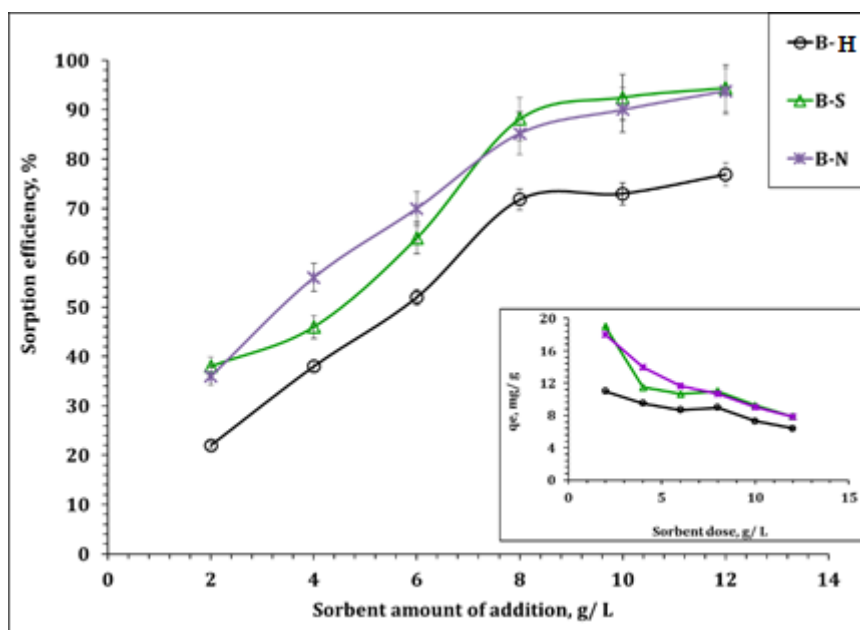


Figure (5): Effect of the amount of adsorbents, g/l, on the iron adsorption efficiency clays, wastewater using different activated Bentonite (adsorption time 450 min, temperature 20 ± 1 °C, 400 rpm).

3.2.4. Effect of temperature

The influence of temperature on the iron adsorption onto the clays from waste water was carried out at 4 different temperatures ranging from 25 to 50 °C at solid/ liquid ratio, 0.12 g/ 15 mL, and adsorption time of 720 min. The obtained data are given in (Figure 6) as a relation between iron adsorption efficiency % and

temperature. The obtained results indicate that the removal percentage of iron is 86, 85 and 71% for BS, BN and BH respectively. This decrease in the iron uptake capacity with increasing temperature might be due to a decreasing effect in the surface activity where at higher temperature, the thickness of the boundary layer would decrease due to the increasing tendency of iron to escape to the solution phase, the iron adsorption experiments were carried out at room temperature.

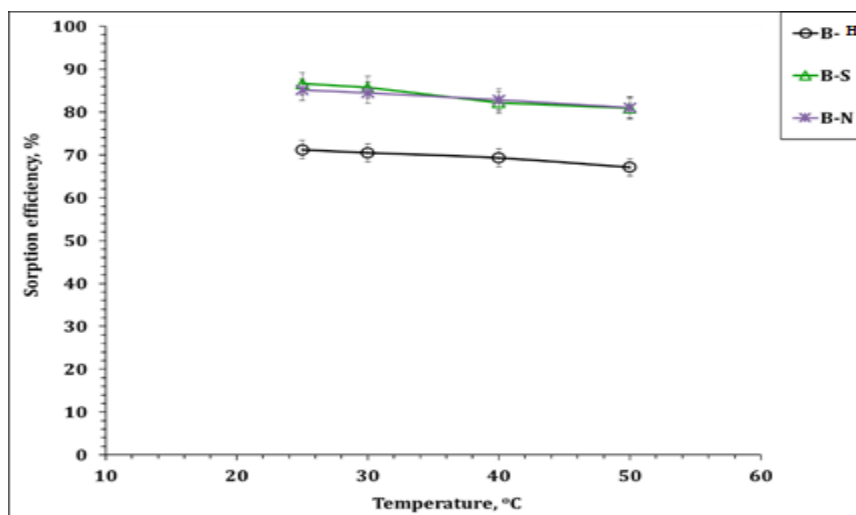


Figure (6): Effect of temperature on the iron adsorption efficiency, % (adsorption time 720 min; 0.12 g/ 15 mL, 100 ppm, 400 rpm).

3.2.5. Effect of iron Concentration

Metal concentration effect on the adsorption onto the clays was investigated. The concentration of iron was in the range of 25 – 400 ppm with the following conditions: adsorption time of 720 min, solid/ liquid ratio, 0.12 g/ 15 mL, PH 2.6 and at room temperature. The obtained data are presented in (Figure 7) as a relation between iron adsorption efficiency % and metal concentration. The experimental results show that the adsorption efficiency is decreased by increasing the concentration of metal. At reached from 98 to 60% at BS, from 94 to 36% at BN and from 88 to 40% at BH.

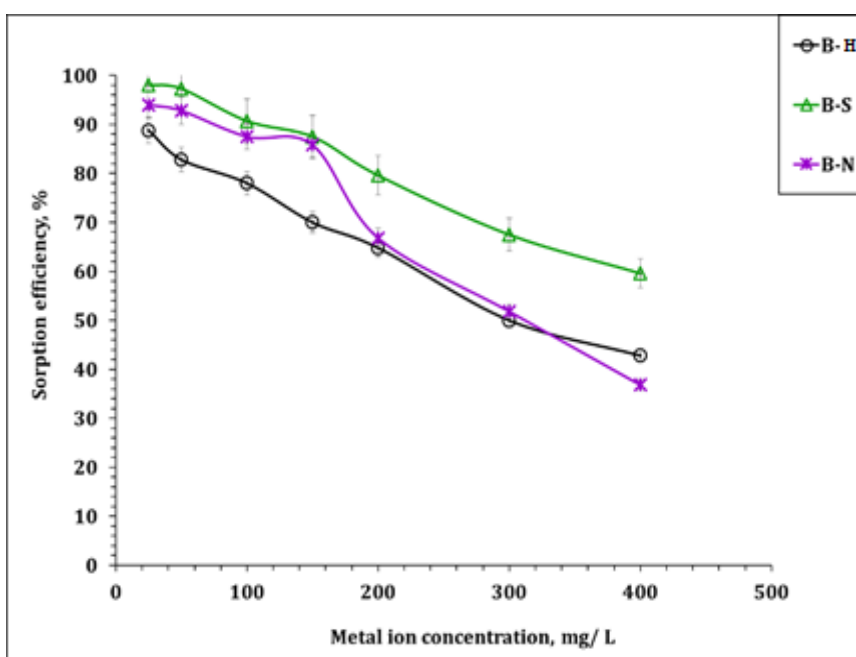


Figure (7): Effect of metal concentration of iron adsorption efficiency from wastewater using different activated Bentonite (adsorption time 720 min; 0.12 g/ 15 mL; room temperature; 400 rpm).

3.2.6. Effect of agitation speed (rpm)

Agitation is an important parameter in adsorption phenomena, influencing the distribution of the clay in the bulk solution and the formation of the external boundary film [20]. The effect of the agitation on the adsorption of iron onto the clays was monitored at several agitation speeds (100, 200,300,400, 500,.. rpm) for 720 min. The results are plotted in (Figure 8) as a relation between Fe adsorption efficiency % and agitation speed. From the results it is clear that, the Fe removal percentage is faintly increased as agitation speed increased. High agitation speed plays a critical role, where it causes a decrease in the boundary layer and so decreases the resistance of transportation. Finally, this enhances the transfer rate of Fe to the surface of the adsorbent, which is called diffusion-controlled mechanism [21].

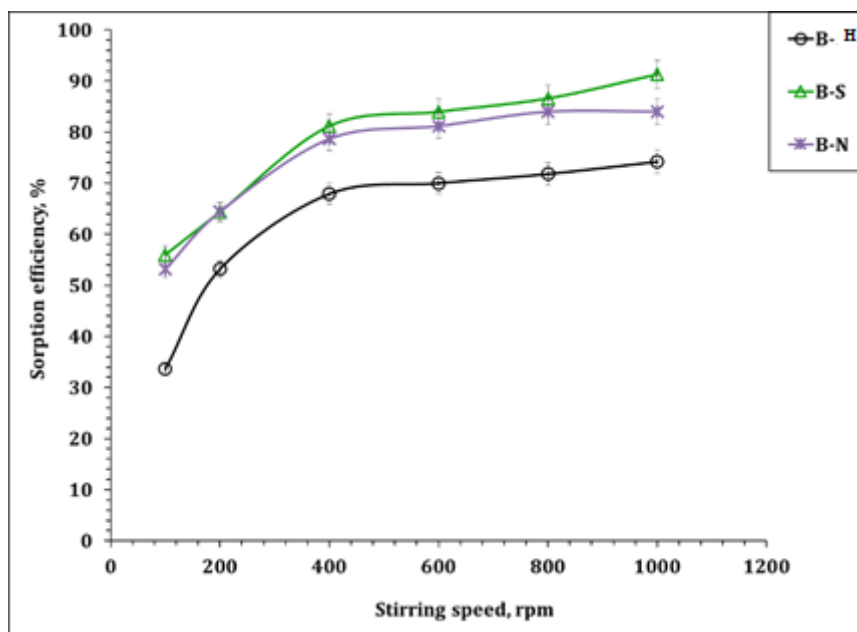


Figure (8): Effect of agitation stirring speed on the iron ion adsorption efficiency, % (shaking time 720 min; 0.12 g/ 15 mL; room temperature).

3.3. Adsorption Kinetic Modeling and Thermodynamics:

3.3.1. Adsorption kinetic modeling

An understanding of adsorption kinetics is important to system design parameters such as residence time, which dictate the physical size and flow rates for many unit operations. The kinetics of physical and chemical reactions can be described by a series of models including: pseudo-first order model and pseudo-second order model.

3.3.1.1. Pseudo-first-order model:

The kinetics of adsorption was analyzed by the Lagergren pseudo-first-order equation [22]:

$$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303} t$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min) respectively. k_{p1} (min^{-1}) is the pseudo-first-order rate constant for the kinetic model. **Figure (9)**

Based on experimental results, linear plot of $\log(q_e - q_t)$ versus time was tested the applicability of Lagergren first order equation to the adsorption of iron. The rate constant was calculated from the slope. The effect of Fe concentration on rate constants (k_{p1}) helps to describe the mechanism of Fe removal from high strength phosphoric acid.

3.3.1.2. Pseudo-second-order model:

The pseudo-second order equation [23] is depicted as follows;

$$\left(\frac{t}{qt}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t)$$

Where k_2 is the rate constant of pseudo second-order adsorption ($g\ mg^{-1}\ min^{-1}$).

The plot of (t/q_t) versus (t) of equation pseudo-second order should give a linear relationship from which q_e and (k_2) were determined from the slope and intercept of the plot, respectively. **Figure (10)**

The plots of Lagergren Pseudo-first-order, Pseudo-second-order, for Fe adsorption from polluted water, 100ppm, using BS, BN, and BH clays. From the figures a linear relationship was obtained and the parameters of kinetic models with the linear correlation coefficients (R^2) of each plot are listed in **(Table 3)**.

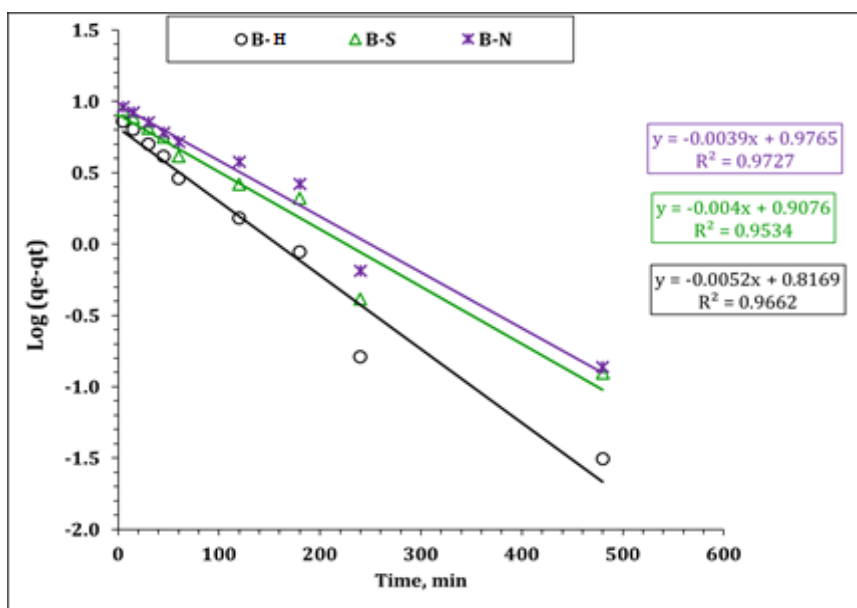


Figure (9): Lagergren plot for iron adsorption from wastewater onto activated bentonite.

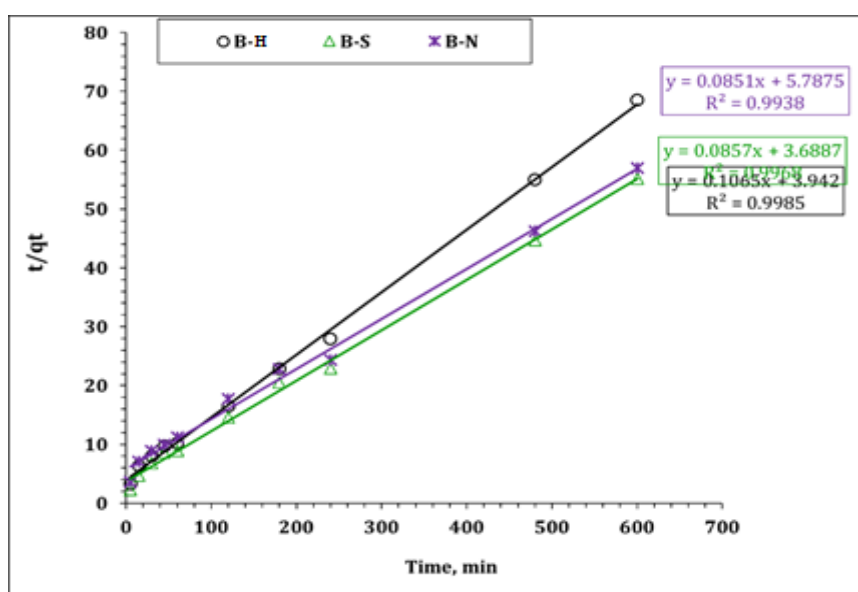


Figure (10): Pseudo- second -order plot for iron adsorption from wastewater onto activated bentonite

Table (3): The calculated parameters of the kinetic models with the linear correlation coefficients (R^2) of each plot

		B-H	B-S	B-N
Lagergreen pseudo first-order	k_1 (min ⁻¹)	0.012	0.009	0.009
	$q_{e_{cal}}$ (mg/ g)	6.6	8.1	9.5
	$q_{e_{exp}}$ (mg/ g)	8.8	10.9	10.5
	R^2	0.96	0.95	0.97
Pseudo second-order	k_2 (min ⁻¹)	0.003	0.002	0.001
	$q_{e_{cal}}$ (mg/ g)	9.4	11.7	11.8
	$q_{e_{exp}}$ (mg/ g)	8.8	10.9	10.5
	h (mol g ⁻¹ h ⁻¹)	0.27	0.23	0.17
	$t_{1/2}$ (h)	34.6	49.9	68.0
	R^2	0.99	0.99	0.99

From the results shown in (Figures 9- 10), it is clear that the Lagergren first order model give straight-line plots for Fe adsorption onto chemical activated bentonite with an average correlation coefficient of 0.96, but the calculated values of q_e dramatically differ from the experimental q_e values. This means that the kinetic of the adsorption process for BN will follow this model, however the others clays not follow even if it gives high correlation coefficient [23].

The pseudo second-order model gives straight-line plots for iron adsorption onto natural and chemical activated bentonite with an average correlation coefficient of 0.99. By comparing the calculating q_e values for the second order models with the experimental value of q_e it is found that the calculated q_e values are close to the experimental q_e values for activated clays which confirm that the adsorption process is more appropriately followed the pseudo-second order model.

3.4. Adsorption Isotherms

3.4.1. Langmuir Isotherm

According to the Langmuir model, adsorption occurs uniformly on the active sites of the sorbent, and once a sorbate occupies a site, no further sorption can take place at this site. Thus, the Langmuir model is given by the following equation. [24, 25]

$$C_e/q_e = 1/bQ_0 + C_e/Q_0$$

where Q_0 and b , the Langmuir constants, are the saturated monolayer sorption capacity and the sorption equilibrium constant, respectively. A plot of C_e/q_e versus C_e would result in a straight line with a slope of $(1/Q_0)$ and intercept of $1/bQ_0$ as seen in Fig. 11. The Langmuir parameters given in Table 3 can be used to predict the affinity between the sorbate and sorbent using the dimensionless separation factor R_L [26,27],

$$R_L = 1 / (1 + bC_0)$$

R_L value indicate the type of isotherm to be irreversible ($RL = 0$), favourable ($0 < RL < 1$), linear ($RL = 1$) and unfavourable ($RL > 1$)[28,29]. The values of R_L for adsorption of Fe onto activated bentonite are shown in Fig. 12, which indicate that adsorption of Fe is more favorable at higher initial Fe concentrations than at lower concentrations.

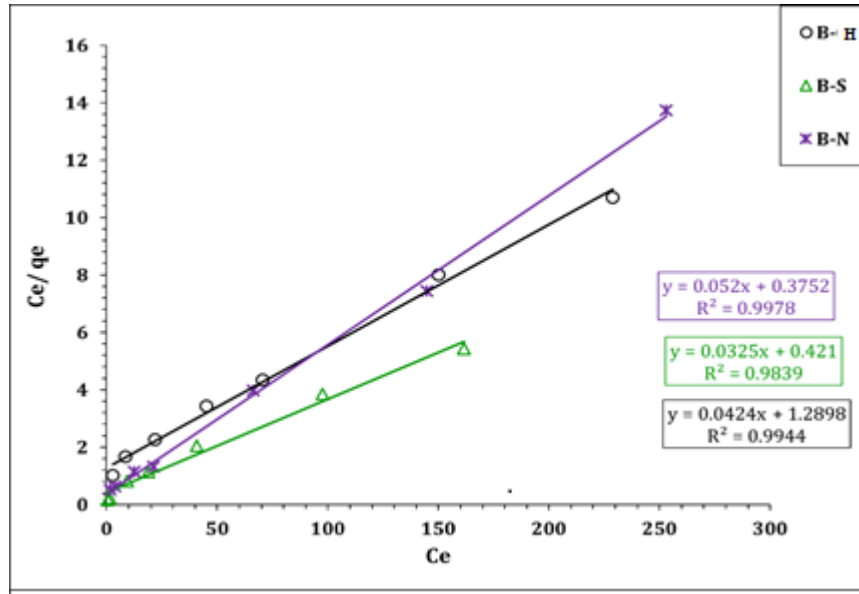


Fig.(11): Langmuir isotherm plots for adsorption of iron onto Activated bentonite.

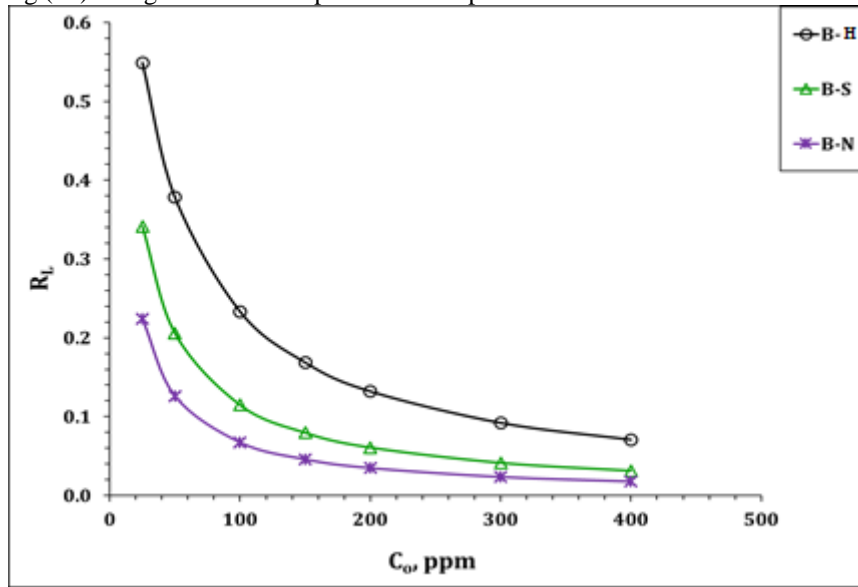


Fig. 12: Separation factor R_L of iron onto Activated bentonite.

3.4.2. Freundlich isotherm

The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of solute adsorbed at equilibrium, q_e , is related to the concentration of solute in the solution, C_e , following [24, 25]:

$$q_e = K_F C_e^{1/n}$$

This expression can be linearized to give

$$\log q_e = \log K_F + 1/n \log C_e$$

where K_F and n are the Freundlich constants, which represent sorption capacity and sorption intensity, respectively. A plot of $\log q_e$ versus $\log C_e$ would result in a straight line with a slope of $(1/n)$ and intercept of $\log K_F$ as seen in Fig. 13. Freundlich constants are given in Table 4.

The experimental data shows that the adsorption of Fe onto activated Bentonite fitted well with Langmuir than Freundlich isotherm.

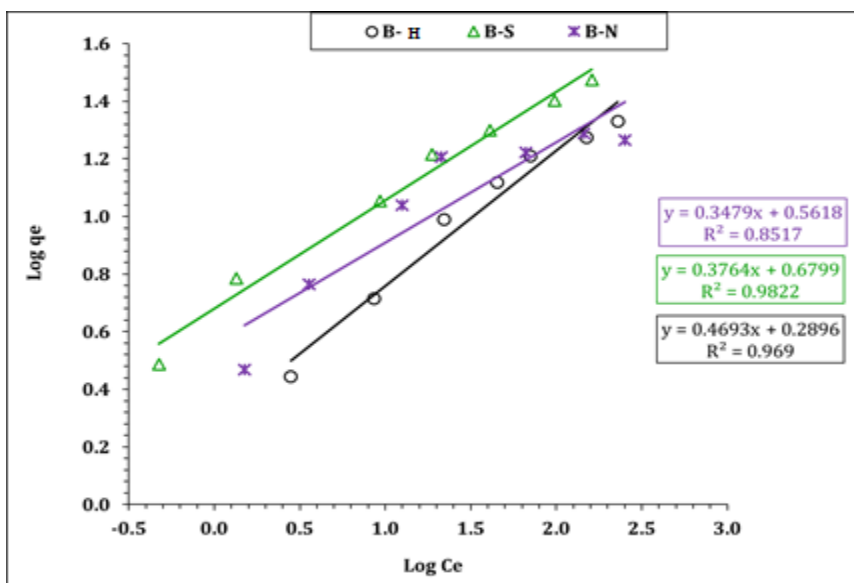


Fig. 13: Freundlich isotherm plots for adsorption of iron onto activated Bentonite

Table 4: Langmuir and Freundlich parameters for iron onto activated Bentonite

		B-H	B-S	B-N	
Freundlich isotherm model	n	2.1	2.7	2.9	
	K_f (mg/ g)	1.9	4.8	3.6	
	R²	0.96	0.98	0.85	
Langmuir isotherm model	Q_m (mg/g)	23.6	30.8	19.2	
	b (L/ mg)	0.03	0.08	0.14	
	R²	0.99	0.98	0.99	
	RL	Co, ppm			
		25	0.549	0.341	0.224
		50	0.378	0.206	0.126
		100	0.233	0.115	0.067
		150	0.169	0.079	0.046
200		0.132	0.061	0.035	
300		0.092	0.041	0.023	
400	0.071	0.031	0.018		

4. Iron de-sorption

The following solutions NaCl, HCl, HNO₃ and CH₃COONa were tested for iron elution from the loaded activated Bentonite. The elution experiments were carried out by three elution circuit by shaking the loaded bentonite sample (0.5g) with three fresh eluent portions (25 ml). A systematic calculation of the eluted Fe amounts was carried out after its analysis in the collected eluate (for each elution solution tested). Table 5 summarizes the obtained data, it is clearly obvious that the NaCl elution solution is the best solution tested as an eluant for iron from the loaded bentonite.

Table 5: Elution yields using different eluent reagents

Eluent type	Elution efficiency, % BS	Elution efficiency, % BN	Elution efficiency, % BH
1.0M NaCl	85.0	88	82.0
1.0M HNO ₃	71.0	74	71.0
1.0M HCl	68.0	80	62.0
1.0M CH ₃ COONa	66.7	22	10.7

5. Case study

A Case study of the sorption results was carried out, using 500 mL from waste water with iron concentration of 150 mg/L contacted with 5 g from activated clay for 720 min. at room temperature (25±2) °C and the pH adjusted at 2.8. After equilibration, the solution was filtered and analyzed for the Fe concentration and it is found that, the total sorption capacity of BS, BN and BH achieved 90,80 and 60% respectively. The sorbed iron desorbed by 1.0M NaCl of both type.

6. Conclusions

The obtained results of Fe adsorption showed that the prepared BS, BN, and BC is an efficient adsorbent for Fe recovery from the waste water. The calculated theoretical capacity was about 30,23 and 19mg Fe/g BS, BC, and BN respectively. We succeeded to elute more than 85, 82 and 88% of the loaded Fe amount on the BS, BN, and BH respectively adsorbent using 1.0M NaCl as an eluent solution.

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