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Research Article **Open Access**

Sorption Characteristics of Iron, Fluoride and Phosphate from Wastewater of Phosphate Fertilizer Plant using Natural Sodium Bentonite

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Abstract

The phosphate fertilizer industry generates a highly hazardous and acidic wastewater. Effluent samples were obtained from wastewater streams produced in Abu Zaabal for Fertilizer and Chemicals Company (AZFC). The present study reports a process for iron, fluoride, and phosphate sorption from the wastewater samples using natural sodium bentonite. Accordingly, a series of batch experiments were performed to study the influence of various experimental parameters, such as solution shaking time, solution pH, and clay amount of addition, temperature, and mechanical stirring speed. The obtained results clear that, the sorption preferred conditions were; shaking time of 60 mts, solution pH of 4, room temperature, and bentonite amount of addition of 1.0 g/L. Based on kinetic and thermodynamic studies, the sorption process of iron, fluoride and phosphate on Na-bentonite is said to follow pseudo-second order mechanism and endothermic nature.

Keywords: Sorption; Wastewater; Phosphate; Fertilizer plant; Sodium bentonite

Introduction

The rapid increase in the world's population is the main driving force for the growing demand for agricultural products in the form of food and fuel. So there is need for reclaiming more land for crop production but its cost is too high, so this demand can be met mainly by increased production on existing crop land by using chemical fertilizers. So as this demand has increased, the demand of phosphate fertilizer has increased [1].

Phosphate fertilizers are produced by adding acid to ground or pulverized phosphate rock. If sulfuric acid is used, single or normal, phosphate (SSP) is produced, with a phosphorus content of 16-21% P_2O_5. If phosphoric acid is used to acidulate the phosphate rock, Triple Phosphate (TSP) is the result. TSP has a phosphorus content of 43-48% as P_2O_5. The phosphate fertilizer plant used millions of gallons of water introducing phosphoric acid and solid phosphate fertilizers. Phosphate fertilizer industries produce a particular kind of effluent which is highly acidic (pH=2) and contains significant amounts of pollutants such as: fluoride, phosphate, and other elements [2-4]. These pollutants are mainly present due to the use of rock phosphate. The high content in these pollutants and the enormous daily flow-rate of fertilizer industry wastewater from phosphoric acid and/or Triple Superphosphate (TSP) production lead to the discharge of several thousand tons of these elements per year [2,3]. Thus, Wastewater treatment is a major problem in such complex fertilizer plant from the environmental pollution point of view.

Considering the growing environmental, economical, and technical concerns regarding fertilizer industry wastewater treatment, a variety of treatment strategies have been developed to reduce the contamination in pond water to facilitate reuse or discharge [5,6]. Usually the industrial wastewater treatment employs one or more processes from physical, physico-chemical and biological methods. Conventional technologies for the removal of heavy metals such as chemical precipitation, ion exchange, electrolysis, and reverse osmosis are often neither effective nor economical. Among the physicochemical treatment, adsorption technique is cheap, effective, and easy to adapt [7].

Clay materials are one of the low-cost natural adsorbent materials that may be used as ion exchangers for the removal of heavy metals from water [8]. Bentonite is alumina-silicate clay mineral, which has been used, in metal absorption because of its physicochemical properties i.e. large specific area, high cation exchange capacity and strong absorptive affinity with organic and inorganic substances, low cost and low permeability [9]. Bentonite is generally classified according to its dominant exchangeable interlayer cation, either sodium or calcium, although magnesium may also be present. Sodium bentonite is the name for the ore whose major constituent is the mineral, sodium montmorillonite. Montmorillonite are three-layer minerals consisting of two tetrahedral layers sandwiched around a central octahedral layer (Figure 1).

Concerns about sustainable removal and recycling of these pollutants have resulted in research into efficient means and strategies to help control and mitigate their effects [5,6]. Application of novel approaches in the wastewater treatment practice will not only improve the Effluent Treatment Plant (ETP) operation for better performance at reduced cost, but also provide an incentive for recovering part of the cost of treatment. In this contribution and regards to environmental aspect, this paper aims to investigate the treatment of wastewater streams-produced during fertilizer manufacture process using Na-bentonite by batch kinetics and equilibrium studies.

Experimental

Materials and reagents

Natural sodium bentonite (Na-B) was obtained from Egypt

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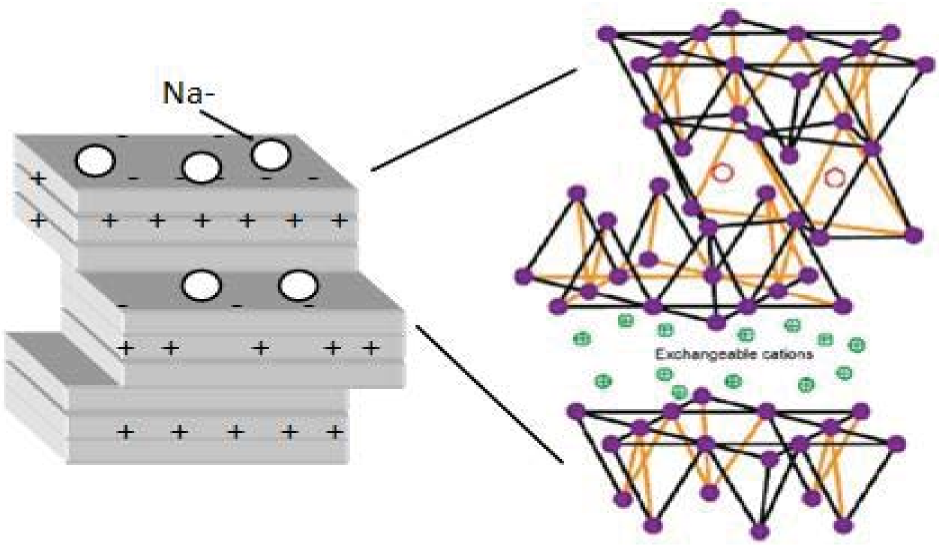

Figure 1: Crystalline structure of sodium bentonite with inter lamellar water layer [10].

Bentonite &Derivatives Company (EBDC), Egypt. The provided natural sodium bentonite sample was crushed, ground in a mortar and sieved to the used grain size of 80 µm. The bentonite sample was purified by water gravitational sedimentation. The washed solid clay sample was dried in electric furnace at 110°C until complete dryness.

Collection of wastewater sample

Wastewater sample was obtained from Wastewater Lake; which used for collecting wastewater streams produced during fertilizer manufacture process in Abu Zaabal for Fertilizer and Chemicals Company (AZFC). The wastewater sample was preserved in refrigerator at 4°C for further use, therefore the potential for volatilization or biodegradation of the sample can be minimized. The chemical analysis of the wastewater sample is given in Table 1 as analyzed in the central laboratory of AZFC Company.

Note (What is COD in Table 1? This is abridgement for (chemical oxygen consumed) this is important in waste water analysis because this is indicating for pollution range in the water.

(SO_4): refer to sulfate group in waste water, Abu Zaabal for Fertilizer and Chemicals Company (AZFC) one of companies refactoring sulfuric acid.

Components	Concentrations
pH	3.4
Turbidity (NTU)	150
Conductivity (µmho/cm)	10560
T.S.S (mg/L)	610
T.D.S (mg/L)	13200
COD (ppm)	290
Total hardness (ppm)	6500
P (ppm)	1120
SiO^2 (ppm)	1751
SiO^4 (ppm)	512
Cl^- (ppm)	205
F^- (ppm)	3400
Fe (ppm)	310

Table 1: Chemical analysis of the wastewater working sample.

Na-Bentonite characterization

Mineral composition: The mineralogical analysis of bentonite sample has been carried out by using a powder X-ray diffractometer (model XD1180, Schimadzu, Japan) equipped with a copper target Cu Kα radiation under target voltage 40 kV and current 30 mA in (a scanning rate of 2°C/min).

Chemical composition: The elemental analyses of bentonite sample have been performed by X-ray Fluorescence (XRF) using Philips PW-2400 sequential X-ray spectrometer (Japan).

Fourier transform infrared (FTIR) spectrum: The identification of the surface functional groups of bentonite sample were carried out in the mid-infrared region from 4000 to 500 cm^{-1} with PerkinElmer Spectrum BX Infrared spectrometer under ambient air condition using KBr as diluent.

Surface area: The specific surface area of bentonite sample was measured by BET method using Nova 2000 quantachrome. The moisture and gases on the solid surface or the penetrated in the open pores were removed by heating at 120°C for 2 hrs prior to the surface area measurements.

Apparatus

The reaction was carried out in a cylindrical 250 ml reactor of 10 cm diameter. It was fitted with Teflon-coated stirrer with 2 cm 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.

Experimental procedures

Unless otherwise stated, Batch adsorption experiments were performed by shaking 1.0 g of natural Na-bentonite with1000 mL of the wastewater in a thermo stated shaker bath at (25 ± 1°C). After the corresponding time interval, the solutions were filtered through a 0.45 μm pore size membrane. Iron and phosphate ions concentration in the filtrate was determined using an inductively coupled plasma optical emission spectrometer (Optima 2100 DV, Perkin-Elmer). Fluoride concentration in the filtrate was measured by a Fluoride ion selective electrode (Thermo Scientific Orion Star A215 pH/ Conductivity Bench top Meter (USA) coupled to an 8157BNUMD Orion ROSS Ultra Triode pH/ATC electrode). The sorption capacity (qe, mg/g) was calculated using the following equation:

$$q_e=(C_o-C_e) \times V/m \qquad (1)$$

Where, C_o and C_e are the initial and equilibrium concentrations of iron, fluoride, and phosphate ions (mg/L), respectively, V is the volume of the wastewater (L), and m is the weight of clay used (g). The removal efficiency (R) of Fe, P, F ions from working waste solution was calculated as follows:

$$R\%=(C_o-C_e)/C_o \times 100 \qquad (2)$$

The distribution coefficient (K_d) of iron, fluoride, and phosphate ions between the aqueous bulk phase and the solid phase was calculated through the following equation:

$$K_d=(C_o-C_e)/C_o \times V/m \qquad (3)$$

Results and Discussion

Characterization of raw materials

XRD study: X-ray diffraction is a nondestructive analytical technique, which reveals information about crystallographic structure. The XRD pattern of the bentonite working sample was shown in Figure 2. From the Figure 2, it is found that the natural bentonite sample contains a sodium-rich montmorillonite (NaM) as the dominant clay mineral [11]. Montmorillonite seems well crystallized in the sample. Other minerals such as: Quartz and Feldspar were found as clay mineral impurities.

XRF analysis: Chemical composition of natural bentonite was summarized in Table 2. From the obtained results, it is found that natural Na-bentonite sample is composed mainly of silicon dioxide, aluminum oxide, and iron oxide, in addition to sodium, potassium, calcium, and magnesium oxides. The obtained analysis showed that the Al_2O_3/ SiO_2 ratio was about 1/3 as expected for montmorillonite which is the main component of bentonite under study. The contents of CaO and Na_2O (K_2O) reflect interlayer cation in montmorillonite. Different contents of CaO and Na_2O can classify the kind of bentonite as either Ca-bentonite or Na-bentonite. The obtained results, clear that the ratio of {(Na_2O+K_2O):(CaO+MgO)} for the working sample was found to be (3.78%:3.46%) by sequent confirming that the natural bentonite sample belongs to Na-bentonite category [12]. And also the wt. % of Na_2O (%) was found to be higher than (CaO) (%) this revealed to this type of Na-bentonite.

FTIR Study: FTIR spectra of Na-bentonite sample has been presented in Figure 3a. The results of IR spectroscopy of clay sample shows the characteristic bands of bentonite at 362 cm^{-1} and 914 cm^{-1} (corresponding to dioctahedral semectites); at 3697 cm^{-1} (corresponds to semectite); at 535 cm^{-1} (Al–Al–OH stretching vibration of the octahedral semectite); at 441 cm^{-1} (Si–O–Al and Si–O–Mg); at 912 cm^{-1} (Al–Al–OH bending vibration); at 795 cm^{-1} (Mg–Fe–OH bending vibrations of illite); at 3697 cm^{-1} and 795 cm^{-1} (Al–OH–Mg); and weak band at 770 cm^{-1} (Fe^{+3}–OH–Mg) but after sorption of wastes, some bands disappeared (Figure 3b); such as that bands of Si–O–Al, Si–O–Mg stretching frequency, and Si–O bending frequencies, in addition, the deep band at 1034 cm^{-1} of Si–O–Si stretching frequencies. This is due to the binding of metal ions mainly located on the clay lattice region, so basically affected the Si–O vibrations. In addition, there was

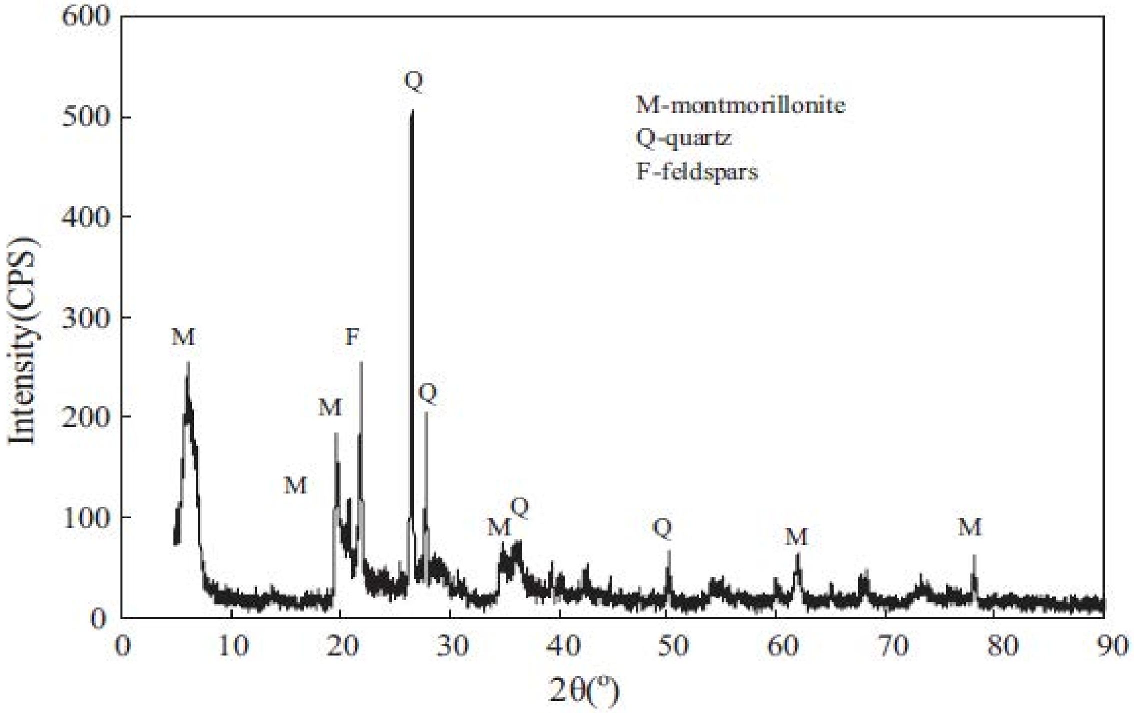

Figure 2: XRD of Na-bentonite sample.

Oxides	Wt%
SiO_2	54.91
TiO_2	1.53
$Al2O_3$	17.01
$Fe2O_3$	9.31
MnO	0.08
MgO	2.47
CaO	0.99
Na_2O	2.75
K_2O	1.03
P_2O_5	0.16
Cl	1.20
SO_3	0.48
L.O.I	8.06

Table 2: Chemical composition of the working Na-bentonite sample.

a strong broadening band of water, which may be due to the moisture after adsorption experiments.

Surface area: The determined surface area of natural Na-bentonite sample was determined through the BET method. The obtained results clear that the specific surface area (S_{BET}) and the total pore volume (V_T) of the clay sample were 33.02 m^2/g and 0.0583 cc/g respectively. This value indicates that there is a large surface area, and hence more available active sites (Figure 4).

Batch Investigation

The effect of different parameters on the sorption behavior of Na-bentonite has been investigated, by batch technique, in order to get the optimum sorption conditions for Fe, P, and F ions removal from wastewater. These parameters include solution shaking time (5-240

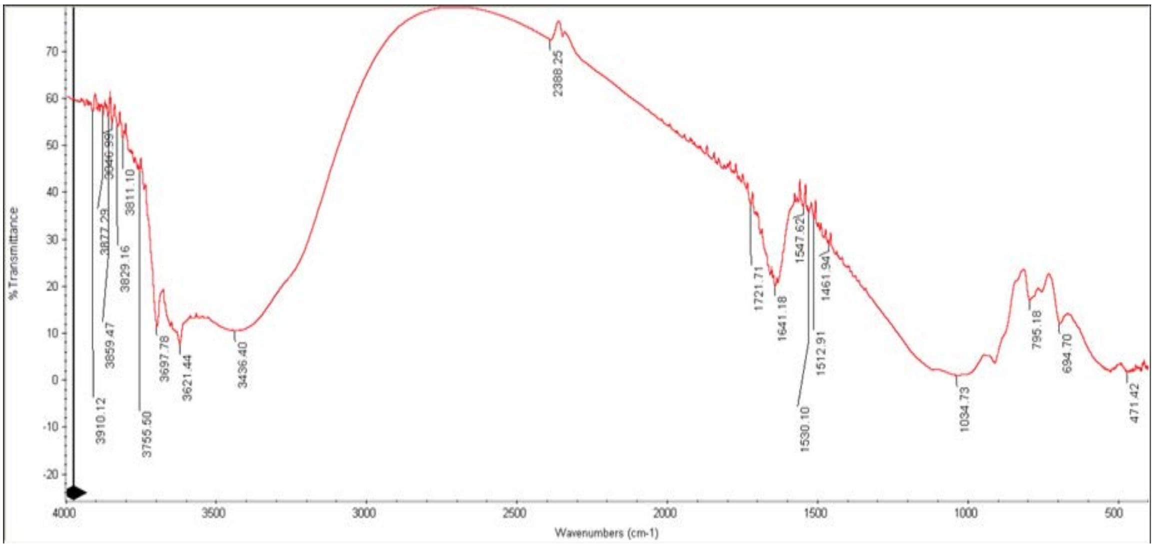

Figure 3a: FT-IR spectrum of Na-bentonite before sorption.

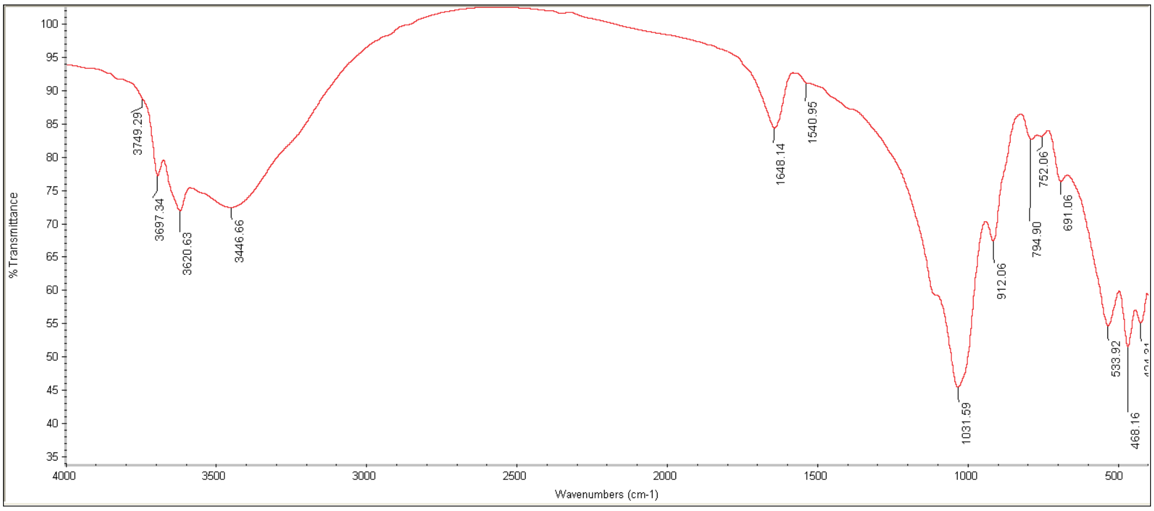

Figure 3b: FT-IR spectrum analysis of Na-bentonite after sorption.

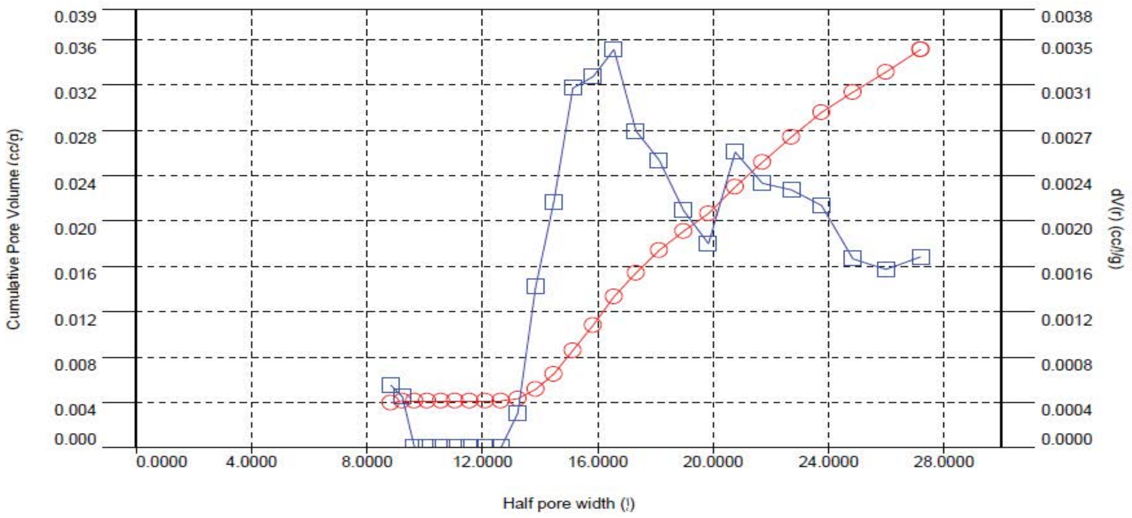

Figure 4: relation between cumulative pore volume and half pore width.

min), solution pH (2-10), clay amount of addition (0.25-2.5 g/ L), temperature (25-65°C), and mechanical stirring speed (25-100 rpm).

Effect of sorption time: A proper amount of Na-bentonite (1.0 g/ L) was shaken with wastewater sample to investigate the kinetic of Fe, P and F ions sorption efficiency as a function of shaking time. The reaction time was ranging from 5 to 240 min while other experimental parameters were solution pH of 4, stirring speed of 65 rpm, and sorption temperature of 25 ± 1°C. The results (Figure 5) indicated that Fe, P and F ions sorption efficiency improved with increasing the shaking time until a steady state (equilibrium) of sorption is attained after about 30 min for P and F ions, and 60 min for Fe ions. Increasing the negative charges on bentonite surface lead to increase the Fe adsorption in time and amount of adsorption more than P and F until fill all free sites on bentonite surface.

This could be attributed to the availability of the Na-AB surface area, the large number of vacant binding sites [13,14]. Further increase in contact time brings no significant increase in sorption percentage. This means that, the adsorption of all three ions was fast and reached equilibrium within 60 min. The fast equilibrium for the three ions (60 min) will improve the wastewater treatment process by reducing the capital and operational costs. Therefore, the application of Na-bentonite will provide an economic advantage for the large- scale wastewater treatment for the fertilizer production units streams [15]. 60 min was suitable for all subsequent batch experiments.

Effect of pH: The sorbate solution pH is announced to have an essential influence on the sorption tendency of a specific sorbent [16]. A slight change in pH not only influences the metal ion speciation in solution but also the concentration of competing hydrogen ions and the surface chemistry of the sorbent which in turn influences the sorption operation [17]. In this regards, the effect of solution pH ranging from 2-10 on the Fe, P and F ions sorption using Na-bentonite from wastewater has been investigated by shaking 1.0 g of the clay sorbent with 1.0 L wastewater for 60 min at temperature of 25 ± 1°C and stirring speed of 65 rpm. A plot of Fe, P and F ions sorption efficiency on the Na-bentonite under investigation versus pH is given in Figure 6.

The results show that, Fe ions sorption efficiency increased from 67.4 to 80.5 by increasing solution pH from 2 to 4, further increase in lead to decrease the sorption efficiency. In case of P and F ions, the sorption efficiency increased from 43.8 to 66.8 for P ions, and from 28.7 to 49.1 for F ions by increasing solution pH from 2 to 6, further increase in solution pH has negative effect on the sorption efficiency. The dramatically drop in the adsorption efficiency by increase solution pH could be attributed to the precipitation of the three ions. Thus, pH of 4 was selected for further sorption studies.

Effect of Na-bentonite amount of addition: Sorption efficiency as a function of clay amount of addition (0.25-2.15 g/ L) was executed on wastewater solution pH of 4, contact time of 60 min, stirring speed of 65 rpm, and temperature of 25 ± 1°C. The experimental data shown in Figure 7 revealed that the sorption efficiency is directly related to the clay amount, i.e. it increases with increasing Na-bentonite amount. The maximum sorption efficiencies reached 80.5, 60.3 and 36.6% for Fe, F and P ions, respectively, when 1.0 g/ L of Na-bentonite was used. This was attributed to increasing the number of binding sites available to catch Fe, F, and P ions [18]. Further increase in the clay amount of addition up to 1.0 g/ L has slightly effect on Fe, F, and P ions, sorption efficiency. This is may be attributed to the higher adsorbent amount creates particle aggregates, which affect the total surface area, and increase the divisional path length [19].

Effect of temperature: The effect of temperature on the sorption of Fe, P, and F ions from wastewater by Na-bentonite was studied in the range 25-65 ± 1°C. The other parameters were fixed at sorbent amount of addition of 1.0 g/ L, solution pH of 4, stirring speed of 65 rpm, and shaking time of 60 min. From the results shown in Figure 8, it is clear that increasing the sorption temperature from 25-65°C leads to slightly increase in the sorption efficiency of Fe, P and F ions. This behavior indicates that Fe, P, and F ions sorption process by Na-bentonite is an endothermic process. Room temperature will be the chosen temperature for the other sorption investigation.

Effect of stirring speed: Stirring speed 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 stirring on the sorption of Fe, P and F ions from wastewater onto Na-bentonite was monitored at several stirring speeds from 25 to 100 rpm. The results have been presented in Figure 9. From

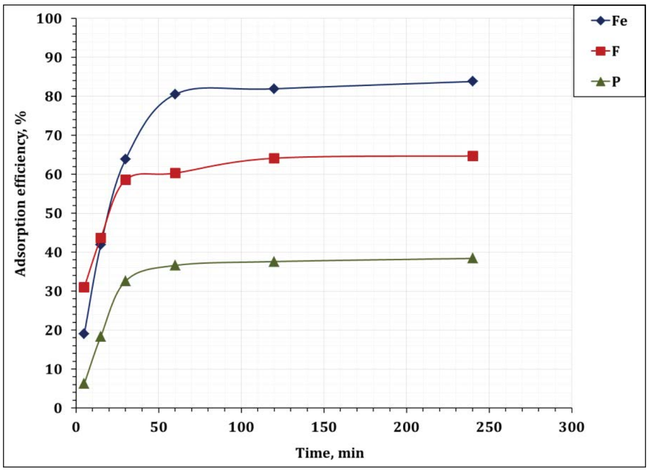

Figure 5: Effect of shaking time on sorption efficiency, % (1.0 g Na-bentonite/ 1.0L, room temperature, 65 rpm, pH4).

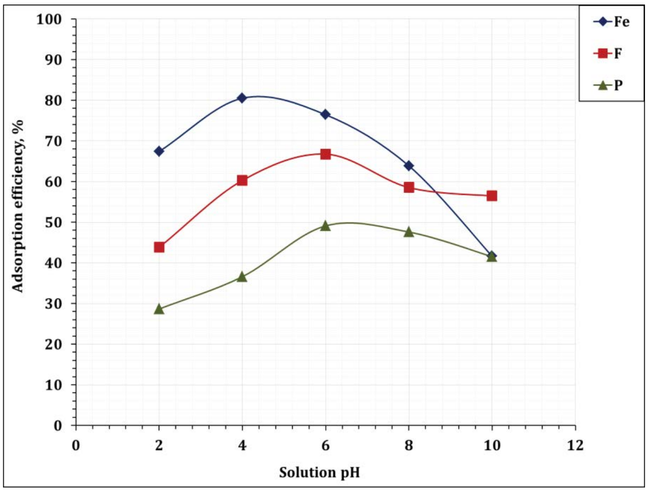

Figure 6: Effect of solution pH on the sorption efficiency, % (1.0 g Na- bentonite/ 1.0L, room temperature, 65 rpm, time 60 mts).

the results it is clear that, the Fe, P and F ions removal percentage from wastewater is faintly increased as the stirring speed increased from 25 to 65 rpm. It means that, 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 metal ions to the surface of the adsorbent, which is called diffusion-controlled mechanism [21]. Further increase in the stirring speed up to 100 rpm has slightly effect on the ions sorption efficiency.

Adsorption kinetic modeling

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Preliminary investigations on the rate of adsorption of Fe, P and F ions from wastewater sample onto Na-Bentonite indicated that the process is kinetically reasonable. From the kinetics study of the adsorption process, it is well recognized that the characteristic of adsorbent surface is a critical factor that affects the sorption rate parameters and the diffusion resistance plays an important role in the overall transport of the solute.

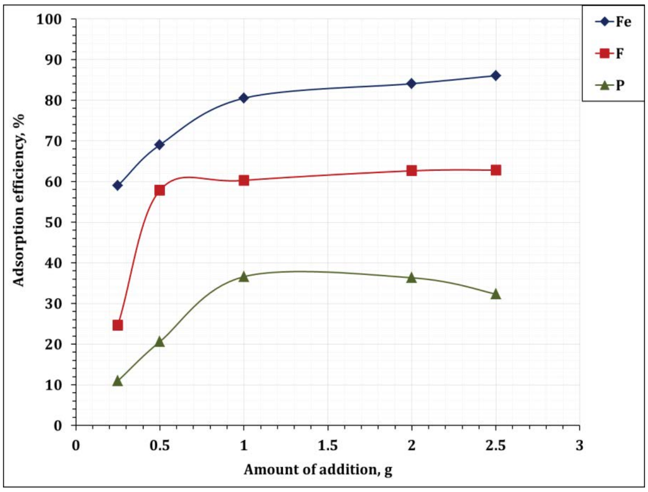

Figure 7: Effect of clay amount of addition, on the sorption efficiency, % (time 60 min, room temperature, 65 rpm, and solution pH- 4).

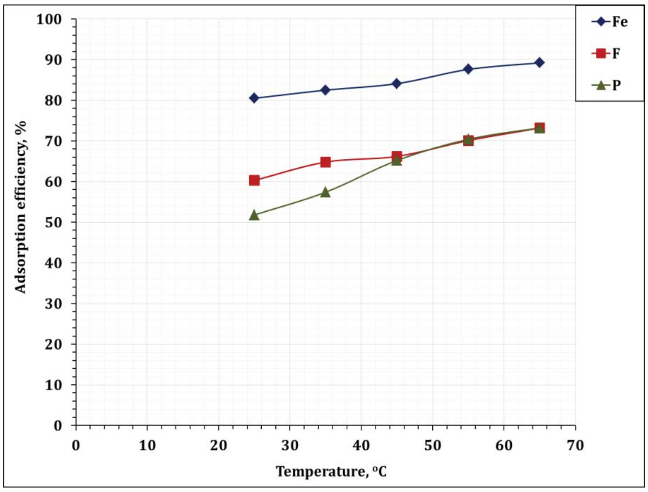

Figure 8: Effect of temperature on the sorption efficiency, % (sorption time 60 min, 1.0 g/ L bentonite clay, 65 rpm, pH 4).

In order to investigate the mechanism of adsorption and rate controlling steps, the kinetic data were analyzed using Lagergren pseudo first order and second order models [22]. The equation of Lagergren was widely used in liquid-solid extraction for sorption of solute from aqueous or organic solution. The Lagergren first order model was given by Equation (4):

$$\log(q_e-q_t)=\log q_e-(k_{p1}/2.303)t \qquad (4)$$

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

The plot of log (q_e-q_t) versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively (Figure 10). The calculated values of k_1 and q_e with the linear correlation coefficients (R^2) of each plot are listed in Table 3.

The pseudo-second order equation [22] is depicted as follows:

$$(t/q_t)=(1/k_2q_e^2)+1/q_e(t) \quad (5)$$

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

Values of k_2 and q_e were calculated from the slope and intercept of the plots t/q_t versus t (Figure 11 and Table 3).

From the results shown in Figures 10 and 11 and Table 3, it is clear that the coefficients of determination (R^2) from pseudo-second order model were 0.99 for the three ions, which are higher than there values in the Lagergren first order model (0.93, 0.95 and 0.88 for Fe, F and P respectively). The real test for the validity of the kinetic model arises from the comparison between the experimentally determined q_e and the calculated q_e [23,24]. It can be noticed that in the pseudo- second-order kinetic model, the calculated qe is very close to the experimental q_e values. Accordingly, the kinetic of Fe, F and P ions adsorption onto Na-bentonite were fitted better with the pseudo-second order kinetic model. This means that the number of adsorption sites on natural Na-bentonite surface and the number of ions in the liquid phase determine the kinetics. This suggests that Fe, F and P ions adsorption from wastewater is chemisorption process which is the result of shares or exchange of electrons between these ions and the functional groups of the bentonite. The obtained results in Table 3 clear that the maximum adsorption (q_e) was observed for Fluoride ions (2200 mg/g), followed by Phosphate ions (430 mg/g) and the lowest one was iron ions (256 mg/g).

Adsorption thermodynamics

The proper assessment of the thermodynamic parameters is considered important to determine the effect of temperature on the adsorption capacity, and to provide information regarding the effect of adsorption process on the inherent energy and structure changes of the adsorbent [25]. The thermodynamic parameters of Fe, P, and F ions adsorption from wastewater acid onto Na- bentonite was determined from the temperature dependent distribution coefficient using Van't Hoff equation (5) of [26].

$$\log K_d = (-\Delta H/2.303R) \times (1/T) + C \quad (6)$$

Where, ΔH is the enthalpy change (KJ/mol), R the universal gas constant (8.314 J/mol K), T is the absolute temperature (K) and K_d is the distribution coefficient of Fe, P, and F ions adsorption, between the aqueous bulk phase and the solid phase.

In this respect, the experimental results obtained were used to calculate the distribution coefficient (K_d), (Figure 12) according to the following equation (7):

$$K_d=(C_o-C_e)/C_e \times V/m \quad (7)$$

According to Van't Hoff equation, the relation between log K_d and 1/T for Na- bentonite will give straight line with from which the enthalpy change, ΔH, can be calculated as shown in (Figure 12). From the Figure straight lines with an average linear correlation coefficient (R^2) of 0.97 were obtained for the three ions. The enthalpy change, ΔH, for the adsorption of Fe, P, and F ions from wastewater onto Na-bentonite was calculated and given in Table 4.

The Gibbs free energy change (ΔG) was also calculated based on the logarithmic value of the distribution ratio Log K_d at the investigation temperature range 25-65°C according to the following equation (8):

$$-\Delta G=2.303\ RT\log K_d \quad (8)$$

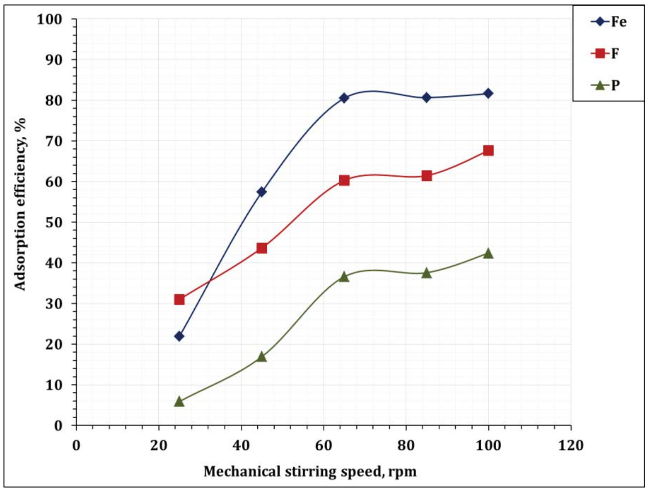

Figure 9: Effect of stirring speed on the sorption efficiency, % (shaking time 60 min, 1.0 g/ L Na-bentonite, room temperature, PH 4).

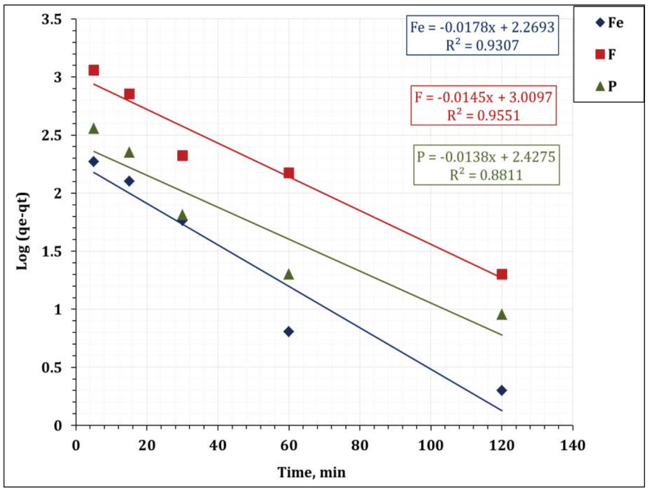

Figure 10: Lagergren plot for Fe, P, and F adsorption from wastewater onto Na- bentonite.

	Lager green pseudo first-order				pseudo second-order			
	K_1 (min^{-1})	qe_{cal} (mg/ g)	qe_{exp} (mg/ g)	R^2	K_2 (min^{-1})	qe_{cal} (mg/ g)	qe_{exp} (mg/ g)	R^2
Fe	-0.02	186	256	0.93	0.0003	270	256	0.99
P	0.03	268	430	0.88	0.0001	476	430	0.99
F	0.03	1023	2200	0.95	0.00006	2500	2200	0.99

Table 3: The calculated parameters of the pseudo first-order and pseudo second-order kinetic models.

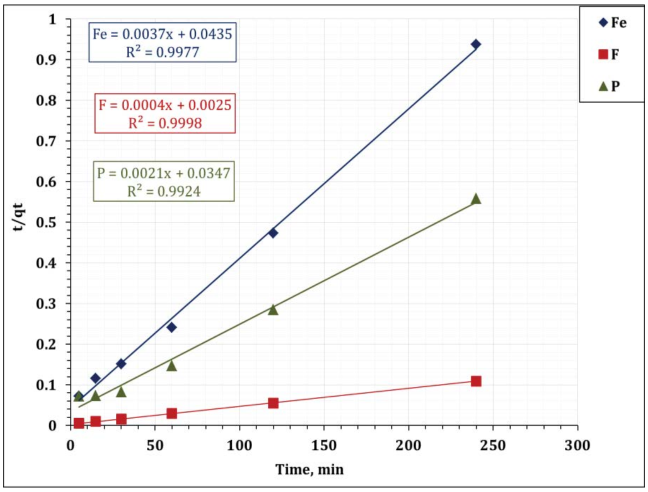

Figure 11: Pseudo second-order plot for Fe, P, and F adsorption from wastewater onto Na- bentonite.

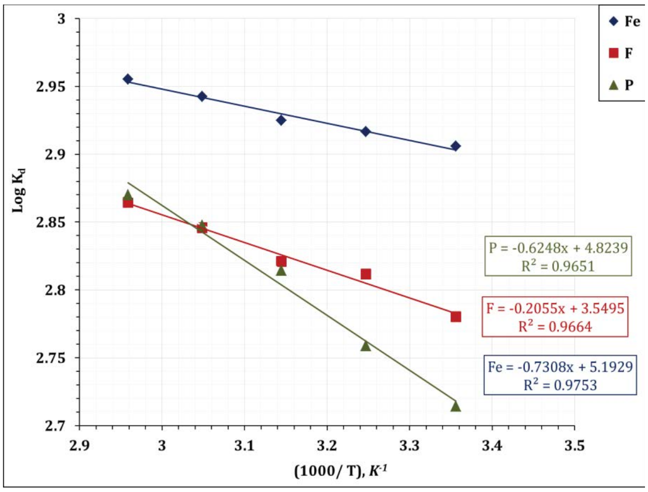

Figure 12: Variation of log Kd with 1/T for Fe, P, and F ions sorption from wastewater onto Na- bentonite.

Also, the entropy change, ΔS was obtained from ΔG and ΔH with the following equation (9):

$$\Delta G=\Delta H-T\Delta S \tag{9}$$

The thermodynamic parameters of the adsorption of Fe, P, and F ions adsorption from wastewater acid onto Na-bentonite are given in Table 4.

From the results obtained in Table 4 it is clear that, the enthalpy change (ΔH) for the adsorption process using Na-bentonite have positive sign which means that the adsorption process is endothermic process. The sign of the enthalpy change (ΔH) associated with the sorption process will consist of (1) enthalpy change for dehydration (ΔH_d) which can be expected to be positive because energy is required to break the ion–water and water–water bonding of the hydrated metal ions, and (2) enthalpy change for complexing (ΔH_c) which will make ΔH more negative due to the formation of metal complex [27].

	ΔG (kJ/ mol)					ΔH	ΔS
	25 °C	35 °C	45 °C	55 °C	65 °C	(kJ/ mol)	(J/ mol K)
Fe	-16.6	-17.2	-17.8	-18.5	-19.1	2.4	64.8
F	-15.9	-16.6	-17.2	-17.9	-18.5	3.91	67.5
P	-15.5	-16.3	-17.1	-17.9	-18.6	7.75	79.3

Table 4: Thermodynamic parameter for Fe, P, and F ions sorption from wastewater into Na- bentonite.

Components	Concentration	
	Before treatment	After treatment
pH	3.4	4
Turbidity (NTU)	150	45
Conductivity (µmho/cm)	10560	4934
T.S.S (mg/L)	610	241
T.D.S (mg/L)	13200	8010
COD (ppm)	290	83
Total Hardness (ppm)	6500	4110
P (ppm)	1120	710
SiO^2 (ppm)	1751	821
SO^4 (ppm)	512	219
Cl^- (ppm)	205	95
F^- (ppm)	3400	1350
Fe (ppm)	310	60.4

Table 5: Chemical analysis of the wastewater working sample before and after treatment with Na bentonite.

Gibbs free energy change (ΔG) values for temperature were found to be negative which mean that the Fe, P, and F ions adsorption from wastewater onto Na-bentonite is feasible and spontaneous process. The higher the reaction temperature, the more negative the value of ΔG, indicating that the adsorption reaction is more favorable at higher temperatures. This behavior could be as a result of that by increase the temperature, the mobility of Fe, P, and F ions in the solution increase and also the affinity of the adsorbate onto Na-bentonite increase [28]. The absolute values of ΔG for Fe, P, and F ions adsorption onto Na-B were smaller than 20 kJ mol^{-1}, which mean that the adsorption process is consistent with electrostatic interaction between adsorption sites and the metal ion (physisorption process) [29].

The positive values of the standard entropy change (ΔS°) for Fe, P, and F ions adsorption onto Na- bentonite indicate that the degrees of randomness increased at the solid-liquid interface with some structural changes at the adsorbent-adsorbate interface which confirming a physical adsorption process [29]. The thermodynamic parameters showed that the Fe, P, and F ions adsorption from wastewater onto Na-bentonite process was feasible, spontaneous and endothermic process.

Sorption process investigation

From the aforementioned adsorption investigation, a sorption experiment was carried out using natural Na-bentonite according to the following preferred conditions; shaking time of 60 min, solution pH of 4, room temperature, and bentonite amount of addition of 1.0 g/L. Within these conditions the Fe, F and P ions sorption efficiencies were 80.5, 60.3 and 36.6% respectively. Accordingly, 1.0 g of natural Na-bentonite was added to 1.0 L of wastewater stream sample and stirring for 60 min at room temperature. After filtration, the obtained solution was analyzed compared with the analysis of wastewater sample as presented in Table 5. From the Table 5, it is clear that the components of the wastewater working sample have been affected by Na-bentonite; where the concentration of these components have been reduced by about 50%. This means that this wastewater stream could be

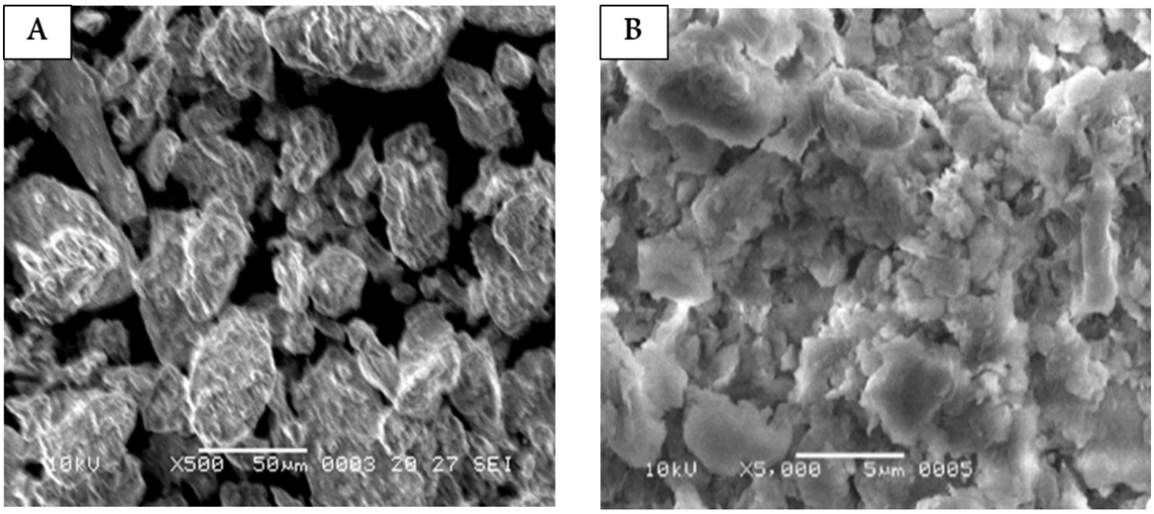

Figure 13: SEM images for bentonite before (A) and after (B) sorption of Fe, P, F ions, respectively.
(A): Pores appears before adsorption and Non- loaded bentonite before adsorption.
(B): Pores disappears after adsorption and loaded bentonite after adsorption.

recycled inside the phosphate fertilizer plan as (gas scrubbers -mixers-in granulation process).

Scanning electron microscope (SEM) analysis is an important tool used in the determination of the surface morphology of an adsorbent. In this study, SEM has been utilized to detect the change in bentonite morphological features before and after the adsorption process (Figure 13). The SEM results showed that the surface morphology of Na-bentonite after adsorption process is different from that of natural Na-bentonite. The natural Na-bentonite showed loose aggregates with a porous structure. After adsorption, the surface of natural bentonite demonstrates compacted aggregates. The surface morphology of the natural bentonite changed interface occurred during the experiment. Similar SEM results were reported by other researchers [30,31].

Conclusions

In the current study, the treatment of wastewater streams produced in Abu Zaabal for Fertilizer and Chemicals Company (AZFC) has been achieved using natural Na-bentonite. The effect of several parameters such as solution shaking time, solution pH, clay amount of addition, temperature, and mechanical stirring speed on the sorption of iron, fluoride, and phosphate has been investigated. The obtained results clear that, the sorption efficiencies of iron, fluoride, and phosphate were 80.5, 60.3 and 36.6% and 67.8% respectively based on the following conditions; shaking time of 60 min, solution pH of 4, room temperature, and bentonite amount of addition of 1.0 g/L. Within these conditions the Fe, F and P ions. Comment on why the adsorption efficiency of Fe ion is the highest, in general bentonite structure allows high adsorption of cations more than anions. The adsorption data obeyed the pseudo-second order kinetic model. The thermodynamics analysis for the wastes adsorption results showed that the endothermic behavior of the process and the thermodynamics parameters (ΔH, ΔG and ΔS) were calculated.

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