



## Research article

## Removal of iron, zinc, and nickel-ions using nano bentonite and its applications on power station wastewater

A.M. Ahmed<sup>a</sup>, Mohamed I. Ayad<sup>b</sup>, Mohamed A. Eledkawy<sup>b,\*</sup>, M.A. Darweesh<sup>c</sup>, Essam M. Elmelegy<sup>d</sup><sup>a</sup> Alexandria University, Faculty of Science, Alexandria, Egypt<sup>b</sup> El-monofia University, Faculty of Science, Egypt<sup>c</sup> Tanta University, Faculty of Engineering, Egypt<sup>d</sup> National Food Safety, Authority, Egypt

## ARTICLE INFO

## Keywords:

Wastewater

Removal of iron, zinc, and nickel

Nano bentonite

Adsorption

Thermodynamic and kinetics parameters

Isotherm models

## ABSTRACT

Removal of high concentrations of toxic heavy metals from wastewater is very important within the environmental field because heavy metals pollution a serious environmental problem due to them being nonbiodegradable. This study shed some light on the use of Nano bentonite as an adsorbent for the elimination of Iron, Zinc, and Nickel ions from wastewater, and the optimum conditions were evaluated to find out thermodynamic and kinetic parameters and equilibrium adsorption models have been applied. The results showed that adsorption percentage increases with increasing temperature, speed of rotation, and volume of solution, but decreases with adsorbent dose and initial concentration increase. The adsorption process has fit pseudo-second-order kinetic model Langmuir and Freundlich adsorption isotherm models were applied to analyze adsorption data and both were found to apply to these adsorption processes. Thermodynamic parameters e.g.,  $\Delta G^\circ$ ,  $\Delta S^\circ$ , and  $\Delta H^\circ$  of the adsorption process were found to be endothermic. Finally, the Nano bentonite was observed to be more powerful for the removal of Fe (III), Zn (II), and Ni (II) at the same experimental conditions.

## 1. Introduction

At the outset, we have to talk about a research and innovation project funded by the Horizon2020 programmer of the European Union and coordinated by the University of Bologna. Its full title is (Development and application of integrated technological and management solutions for wastewater treatment and effective reuse in agriculture tailored to the needs of the Mediterranean countries), this research project was introduced by MADFORWATER [1]. The new technologies developed, that would be adapted to the social and technical context would be able to produce irrigation-quality water from municipal and industrial wastewaters, as that from drainage canals. The MADFORWATER aims to develop wastewater treatment and reuse, improving agricultural production as well as decreasing exploitation of water reserves and water pollution [2]. Adsorption, as the widely used method plays a vital role in wastewater treatment, which is based on the physical interaction between metal ions and sorbents [3]. With the development of nanotechnology, several researchers have proved that nanomaterials are effective sorbents for the removal of heavy metal ions from wastewater due to

their unique structure [4]. Nano Bentonite can be used as an alternative adsorbent because the cost is cheap and abundant in nature and so because the main constituents of Nano bentonite are montmorillonite mineral has a 3-layered structure with a 2: 1 configuration consisting of 2 layers of tetrahedral silica and 1 octahedral layer as a central, the existence of isomorphic substitution in the basic structure causes the formation of negative charges on its surface, this part called the active site which can be used as an adsorbent to bind cations and organic and metallic compounds through electrostatic bonds [5]. The aim of this work is studying the elimination of zinc(II), nickel(II), and iron(III) from wastewater using Nano bentonite as the adsorbent material and make an application of this on some collector samples from the wastewater of electrical power station in Damanhur and wastewater sample collected from one of the major metal coating workshops in Almeria, Alexandria, Egypt. Much work has been done on the removal of zinc, nickel, and iron by different adsorbents such as Nano bentonite is used as an adsorbent [6]. Table 1 shows the maximum % removal of heavy metals with different adsorbents.

\* Corresponding author.

E-mail address: [mohammedeledkawy@gmail.com](mailto:mohammedeledkawy@gmail.com) (M.A. Eledkawy).

**Table 1.** The impact of the use of exceptional adsorbent on the % removal.

Adsorbent	% Removal
Clays [20, 21, 22, 23, 24]	44
Minerals such as goethite [25]	46
Hydroxyapatite [26]	52
Calcite [27, 28, 29, 30]	55
Calcareous soils [31, 32]	45
Sludges [33]	46
Modifedaspaltite ashes [34]	48
Bark, fly ash [35]	54%
Chitosan, dead biomass, modified wool, moss, Peat	~ 56
sea-weed, zeolite, humic acid [36]	60
Sesquioxides (iron, aluminum, or manganese oxides)	60
Hydroxyapatite [24]	62
Nano bentonite [21]	74
Bone char	76
Activated dolomite	80

## 2. Experimental

### 2.1. Materials and reagents

All chemicals used in the study are all analytical grade. Demineralized water used in all preparations, anhydrous ferric sulfate, Zinc sulfate, and Nickel sulfate was used to prepare synthetic  $Fe^{3+}$ ,  $Zn^{2+}$ , and  $Ni^{2+}$ , nano bentonite is used as an adsorbent.

### 2.2. Preparation of nano-bentonite

Bentonite powder about 20 g was dissolved in 100 ml HCl (12M) then heated in a magnetic stirrer at around 343K for 120 min at a speed of 350 rpm. Wash the solution with distilled water repeatedly until the pH is neutral. Oven solution for 5 h with a temperature of 373K. After drying, crushed with mortar to produce a powder. Bentonite powder is calcined in the furnace at 873K. Powder bentonite at a ball mill with a speed of 100 rpm for 30 min and then sieved [7].

### 2.3. Apparatus and instrumentation

A definite volume of metal ion stock solution of (Iron, Zinc, and Nickel) with a known initial concentration is stirred with a definite amount of adsorbent (Nano bentonite) for the stipulated time in digital magnetic stirrer MS-H-Pro with temperature sensor PT 1000 using a Teflon magnetic stirrer bar of 2 cm length. Samples (0.5 ml) diluted to 5 ml by demineralized water and used atomic absorption spectrophotometer model PerkinElmer (PinAAcle 900T) was used to analyze concentrations of the dissolved (Iron, Zinc, and Nickel). pH-Meter GLP 21 Crison instruments were used to adjust the pH of solutions.

### 2.4. Experimental procedures

These experiments were performed by stirring (Nano bentonite) with 200 ml of a dehydrated Ferric Sulfate [ $Fe_2(SO_4)_3$ ], a dehydrated Zinc Sulfate [ $ZnSO_4$ ], and a dehydrated Nickel Sulfate [ $NiSO_4$ ] solutions. Different pH values of the solution ranged from 3-7 were studied. pH was adjusted by using 0.1M of HCL and NaOH. Experiments were carried out at different variables of temperature from 298-323 K, stirring speeds of 100, 200, 300,400, and 500 rpm, Different initial concentration of  $Ni^{2+}$ ,  $Zn^{2+}$  and  $Fe^{3+}$  ions from 50 – 250 mg/l, different volumes from 100 - 350 ml of  $Ni^{2+}$ ,  $Zn^{2+}$  and  $Fe^{3+}$  ions solutions and also (Nano bentonite dosage of 0.01, 0.03, 0.05, 0.1 and 0.3 g/200ml) of the solutions were studied. The samples were taken at regular periods 5, 10, 20, 40, 60, 80, and 120

min. Then they were analyzed using atomic absorption spectrophotometer [8].

### 2.5. Analysis method

The adsorption process of metal ions impacts through many variables (pH, initial concentration, adsorbent dose, contact time, speed of rotation) on the removal of metals, and the effect of different temperatures. The efficiency of the adsorption process can be calculated from the change in % removal value with time; the change in % removal with time was decided from this equation;

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Also, the amount of metallic adsorbed ( $q_t$ ) was acquired from the variations between metal quantity adsorbed by the adsorbent and metallic content of the wastewater sample by the equation;

$$q_t = \frac{(C_o - C_t)V}{m} \quad (2)$$

The amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent ( $q_e$ ) at a fixed temperature at equilibrium called (adsorption capacity) calculated by the equation;

$$q_e = \frac{(C_o - C_e)V}{m} \quad (3)$$

where  $C_o$  (mg/l) is the preliminary metal ions concentration in solution,  $C_e$  (mg/l) is the equilibrium concentration of metal ions within the solution.  $C_t$  (mg/l) is the concentration of metallic ions in the solution after the time (t). m is the mass of nano bentonite used (g), and V is the volume of the solution (ml) [9].

## 3. Results and discussion

The surface area measurement was carried out by the BET method using the Nova 2000 (quanta chrome) instrument obtained Specific surface area of adsorbent nano bentonite is  $119 \text{ m}^2\text{g}^{-1}$ (dry). The crystalline phases in the nano bentonite were characterized with X-ray diffraction (XRD, Philips PW 1750) which indicates the chemical composition of different oxides present in the nano bentonite as shown in Table 2.

### 3.1. FTIR spectra

FTIR measurements were carried out to demonstrate the chemical nature of the nano bentonite and to identify the possible interaction between  $Fe^{3+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$ , and Nano bentonite [10]. The FT-IR spectra of Nano bentonite are shown in Figure 1. The IR absorption bands obtained at  $3632\text{--}3447 \text{ cm}^{-1}$  are ascribed to O–H stretching vibration. The sharp absorption peak at  $1044 \text{ cm}^{-1}$  corresponds to the stretching vibration of the Si–O bond. The peaks at  $466\text{--}624 \text{ cm}^{-1}$  are due to a (Si–O) bending vibration, and the peak at  $796 \text{ cm}^{-1}$  may correspond to the stretching vibration of Al–O–Si. The OH bending bands

**Table 2.** The chemical composition of nano-bentonite.

Oxides present in Nano-bentonite	(wt.%)
SiO <sub>2</sub>	46
SO <sub>3</sub>	23.8
CaO	10.6
Fe <sub>2</sub> O <sub>3</sub>	7.3
AlO <sub>2</sub>	6.4
K <sub>2</sub> O <sub>2</sub>	5.5
Ti O <sub>2</sub>	0.4

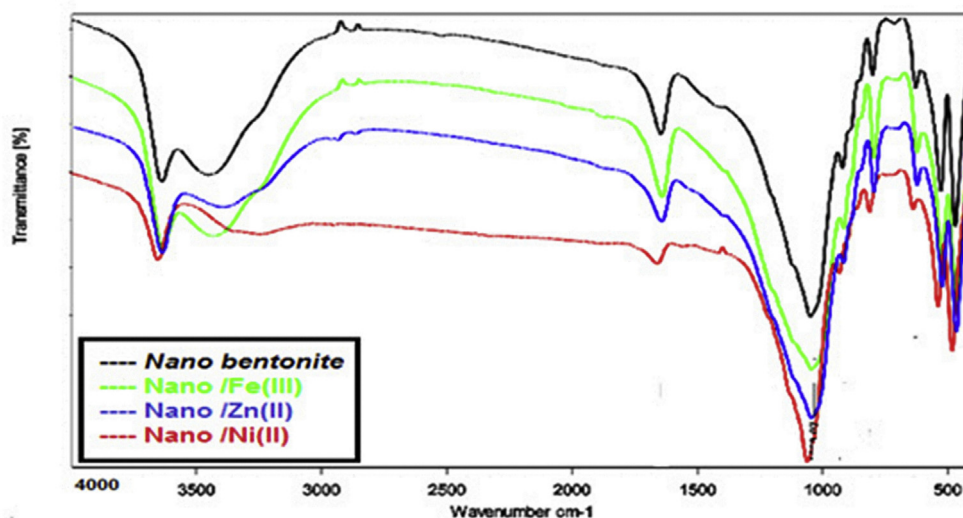


Figure 1. FTIR spectrum for nano-bentonite.

appear at  $916\text{ cm}^{-1}$  [11, 12]. After the adsorbent (Nano Bentonite) was loaded with  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  ions, it was located that there is a difference in the intensity or the places of the absorbance peaks and major change within the FTIR spectra after adsorption of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  ions had been quite similar, this indicated the mechanism for the adsorption of both were the same [13].

### 3.2. Effect of contact time

The effect of contact time was studied, while all other variables such as adsorbent dosage, pH, and initial concentration, the volume of solution, temperature, and rotation speed are kept constant. This method is known as optimization which is based on one factor at a time where one parameter is varied, and the others are kept constant. Figure 2 shows the effect of contact time on % removal that were studied on 0.1 g/200ml of Nano bentonite for initial concentration 50 ppm for  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  values with time and reaches a maximum at 120 min, this indicates that the concentration of Iron, Zinc, and Nickel within the solution decreased rapidly in the first 30 min, and the removal was mainly completed in 120 min. The elimination of metal ions may be derived into changes wherein the removal rate is very high. It is essential to determine the equilibrium time, that is, the contact time characterized by unchanging  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  concentration in the solution was done after a half-hour. For all used different concentrations of solutions; this period is denoted as the second level of the Adsorption. The rate of adsorption of metals at the beginning is high due to the high number of available active adsorbing

sites on the adsorbent surface that is the large uncovered surface area of Nano bentonite [14]. Also, the solid/liquid interface has the highest rate at the beginning of the process, which resulted in fast absorption. Lower slopes of the curves affirm that the second level was a bit lower because of the decrease diffusion speed of metal ions in the pores of the Nano bentonite structure. It may be located that the satisfactory adsorption efficiency was completed in the case of the preliminary solution with the lowest metal ions concentration (50 ppm) [15].

### 3.3. The adsorbent dose effect

Studying the effect of different doses on the elimination percentage of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  ions show that as adsorption percentage decrease with increasing dose of Nano sorbents as we can show a Figure 3, adsorption decreased from (97.9–87.7 %), (98.9–89.7%) and (98.9–87.8%) with an increase in (Nano bentonite) from (0.01–0.3 g/200 ml) for  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  respectively after 120 min [16], this due to increasing the dose of the nano compounds the granules aggregate which leads to decreasing the total surface area and the number of adsorptive sites decreases with increasing the weight of adsorbent (Nano bentonite) which decreases available exchangeable sites which enhance percent of metal ions removal [17]. and, However, with increasing dose of adsorbent the sorption capacity ( $q_e$ ) decrease, indicating the adsorption sites remain unsaturated (It may be due to the following: overlapping of active sites at higher nano-bentonite dosage causing a decrease in the effective surface area resulting in the conglomeration of exchanger particles) [18].

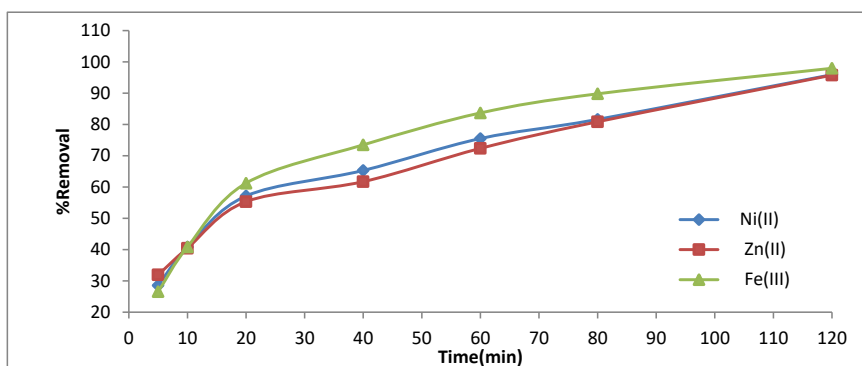


Figure 2. Effect of contact time on the %removal of (Fe(III) at pH = 7) and (Zn(II), Ni(II) at pH = 6), a dose of nano-bentonite 0.1g/200ml solution, 300 rpm, 298 K and 50 ppm at contact time 120 min.

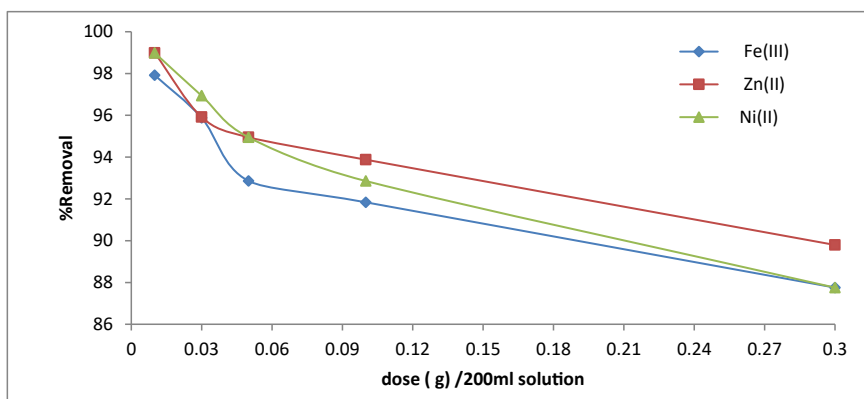


Figure 3. Effect of adsorbent dose (Nanobentonite) on %Removal, initial concentration  $[Fe^{3+}]$ ,  $[Zn^{2+}]$  and  $[Ni^{2+}] = 100$  mg/l ( $V = 200$  ml), 300 rpm and  $T = 298$  K.

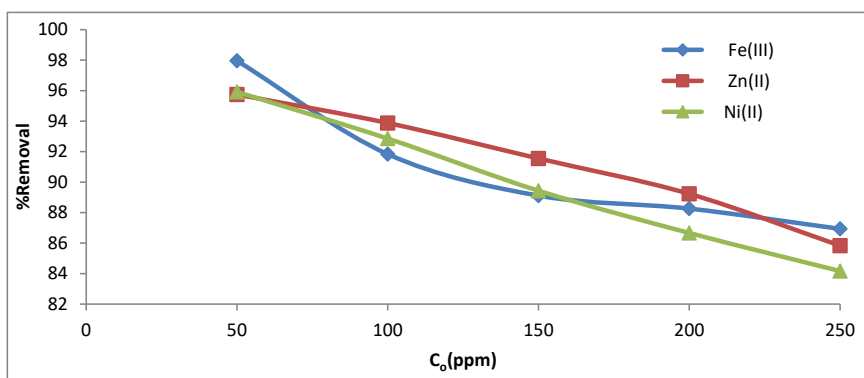


Figure 4. Initial concentration effect on %Removal at constant dose 0.1g of Nano bentonite/200ml solution, 300 rpm,  $T = 298$  K and at 120min. for  $Fe^{3+}$  at  $pH = 7$  and  $Zn^{2+}$ , and  $Ni^{2+}$  at  $pH = 6$ .

3.4. The initial concentration of  $Fe^{3+}$ ,  $Zn^{2+}$ , and  $Ni^{2+}$  effect on adsorption

This study shows the effect of the varying initial concentration of Iron(III), zinc(II), and Nickel(II) solution from 50 to 250ppm on the nano bentonite surface with other fixed parameters the results showed that the adsorption percentage of  $Fe^{3+}$ ,  $Zn^{2+}$ , and  $Ni^{2+}$  ions decreases with an increase of the initial concentration. Presented in Figure 4. At the beginning of the adsorption process of metal ions from an aqueous solution, the surface of the adsorbent is free of metal ions and there are a lot

of active exchangeable sites. Therefore large amounts of  $Fe^{3+}$ ,  $Zn^{2+}$ , and  $Ni^{2+}$  ions species move across from the solution to the nano bentonite surface. The adsorption capacity depends on the concentration of metal ions [19]. This decrease in ions removal percentage could be due to a lack of sufficient active sites on Nano bentonite to adsorb more metal ions available in the solution. So, the percentage of removal depended upon the initial metal ions concentration, and this supports the assumption of the formation of monolayer metal ions on the outer surface of Nano bentonite [20].

Table 3. Adsorption rate constants,  $q_e$  estimated, and correlation coefficient associated with the Lagergren pseudo-1<sup>st</sup> and 2<sup>nd</sup>-order adsorption for the Nano bentonite with iron, zinc, and nickel ions.

Metal ion nano Bentonite	$C_o$ (mg/L)	$q_e$ exp (mg/g)	1 <sup>st</sup> -order model			2 <sup>nd</sup> -order model		
			$q_{ecal}$ (mg/g)	$10^3k_1$ ( $min^{-1}$ )	$R^2$	$10^3K_2$ ( $gmg^{-1}min^{-1}$ )	$q_{ecal}$ (mg/g)	$R^2$
(a) $Fe^{3+}$	50	96	86.9	34.3	0.97	0.525	108.6	0.99
	100	180	238.3	39.2	0.90	0.096	243.9	0.93
	150	262	416.7	41.1	0.83	0.076	333.3	0.96
	200	346	560.6	42.7	0.82	0.063	434.7	0.98
	250	426	660.7	44.3	0.84	0.060	526.3	0.99
(b) $Zn^{2+}$	50	90	89.4	31.6	0.88	0.54	98.0	0.97
	100	184	224.7	36.7	0.83	0.22	204.0	0.96
	150	260	360.2	39.1	0.80	0.13	294.1	0.96
	200	348	544.0	41.4	0.78	0.08	400.0	0.96
	250	412	695.5	42.6	0.76	0.06	476.1	0.95
(c) $Ni^{2+}$	50	94	91.6	32.0	0.89	0.53	103.0	0.98
	100	182	283.0	38.0	0.83	0.09	232.5	0.95
	150	254	448.0	40.0	0.80	0.05	344.8	0.94
	200	338	656.3	42.0	0.79	0.02	500.0	0.93
	250	404	836.2	43.9	0.77	0.01	666.6	0.93

### 3.5. Kinetics of adsorption

The Kinetics study for the adsorption of Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> was completed after 120min for the concentrations (50,100,150,200 and 250 mg/l) of Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> ions onto (0.1g/200 ml) doses of adsorbent (Nano bentonite) at 298K.

Two kinetic models were considered to investigate the mechanism of zinc (II), nickel (II), and iron (III) adsorption onto nano bentonite, as follows:

The pseudo-first-order reaction expression of Lagergren on solid capacity is generally expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The pseudo-second-order model is generally expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where q<sub>t</sub> and q<sub>e</sub> are the amounts of Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> metal ions adsorbed according to unit mass of adsorbent (mg/g) at time t and equilibrium, respectively, and k<sub>1</sub> and k<sub>2</sub> are the adsorption rate constant, the applicability of these two models may be examined via each linear plot of ln(q<sub>e</sub>-q<sub>t</sub>) vs. t for 1st order as shown in (Figure 5 a,b,c) and (t/q<sub>t</sub>) vs. t for 2nd order as shown in (Figure 6 a,b,c). To quantify the applicability of each model, the correlation coefficient, R<sup>2</sup>, was calculated from these

plots. The linearity of these plots indicates the applicability of the two models. However, the correlation, R<sup>2</sup>, showed that the pseudo-second-order model, fits better the experimental data than the pseudo-first-order model, the kinetic parameters calculated are shown in Table 3. The values are near to (q<sub>e exp</sub>) values at different initial concentrations, for the pseudo-second-order kinetics model, the constant rate lower with the growth of initial Iron (III), zinc (II), and nickel (II) concentration [21]. The experimentally determined capacities signifying the ability of the model to predict the experimental data. It can also be seen inside, with an increase in preliminary metallic concentration, the adsorption rate constant k<sub>2</sub> decreases. Near observation was also suggested by the earlier researchers this is due to the lower competition for the sorption surface sites at lower concentrations [22]. At excessive concentrations, the competition for the surface active sites will be high, and consequently, the rate of sorption lowered is obtained [23].

### 3.6. Effect of speed of rotation on the solution of iron, zinc, and nickel ion

Experimental results for the effect of speed of rotation (100, 200, 300,400, and 500 rpm) are presented in Figure 7 The removal of Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup>.reaches 96.9 %, 98.9%, and 97.9% respectively, using Nano bentonite at 500 rpm, it is clear that speed of rotation enhances metal removal from aqueous solutions. This is because metal ions, meet resistance at the liquid phase, through their transportation to the solid phase, through the boundary layer, and with increasing the speed of

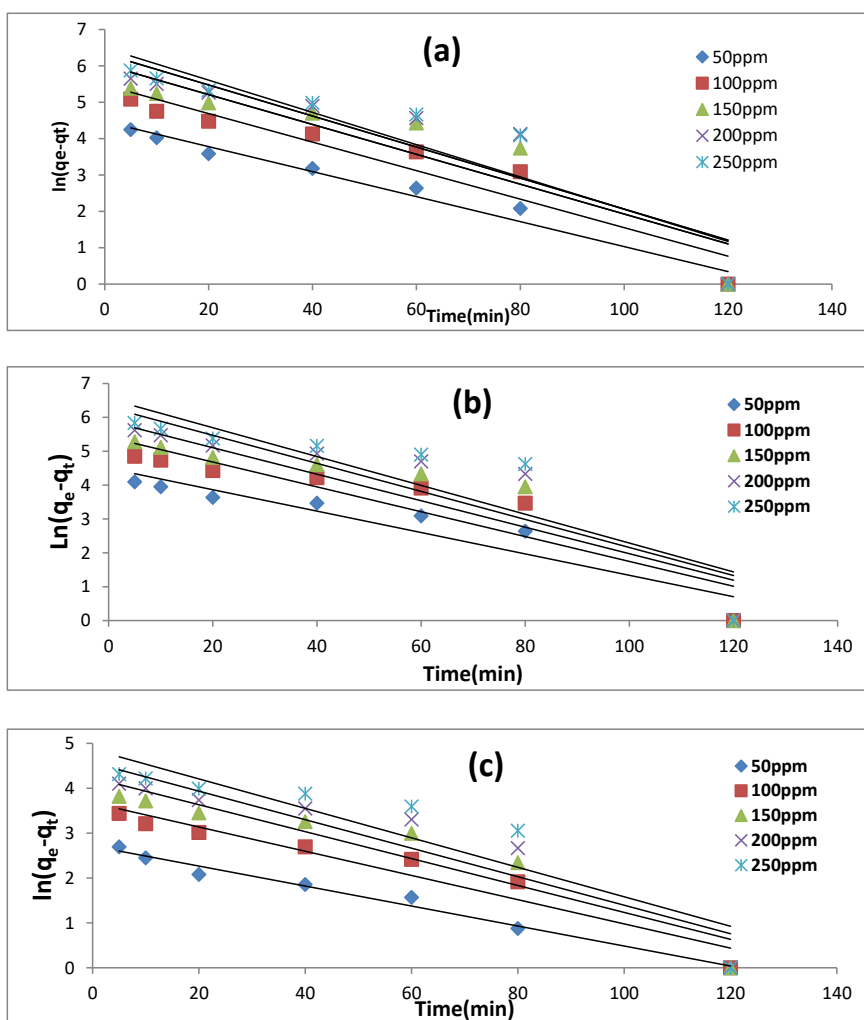


Figure 5. Pseudo-1<sup>st</sup>-order kinetic (a) Fe<sup>3+</sup>, (b) Zn<sup>2+</sup> and (c) Ni<sup>2+</sup> fit for adsorption onto Nano bentonite, 0.1 g/200ml adsorbent dose, 300 rpm and 298k at different initial concentrations.

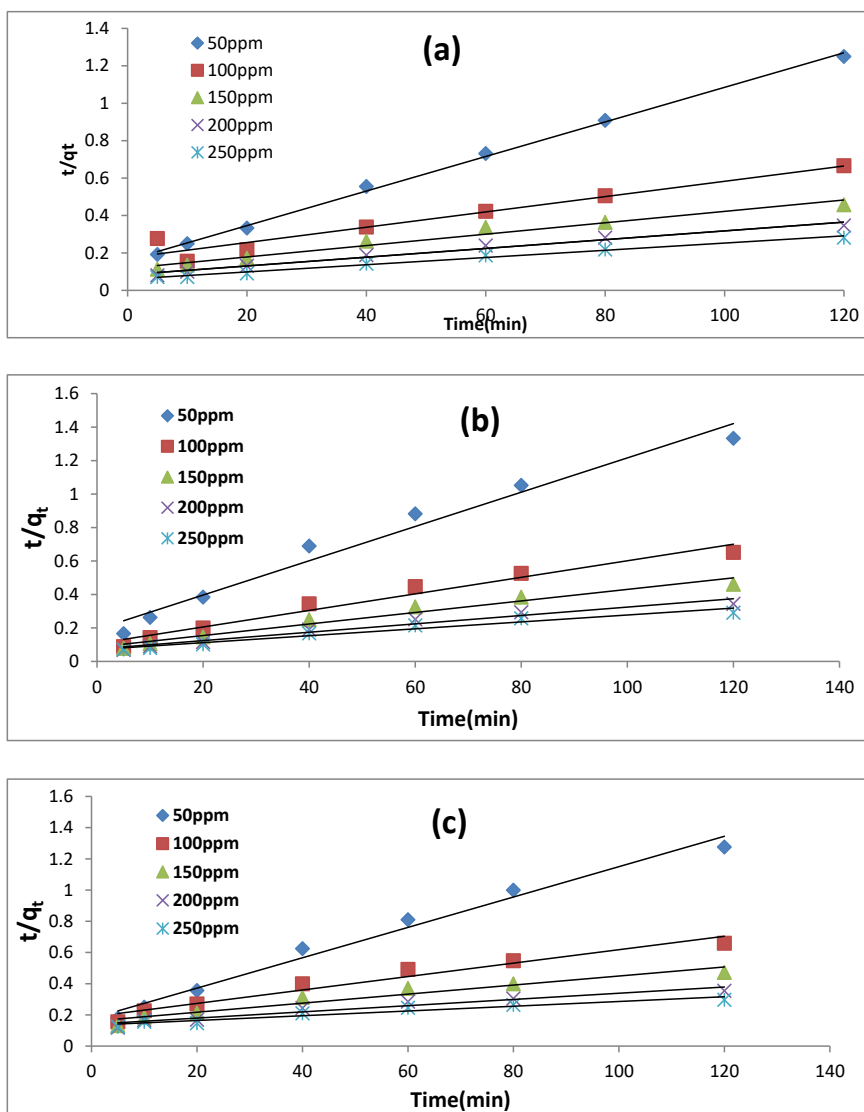


Figure 6. Pseudo-2<sup>nd</sup> order kinetic (a) Fe<sup>3+</sup>, (b) Zn<sup>2+</sup> and (c) Ni<sup>2+</sup> fit for adsorption onto Nano bentonite, 0.1 g/200ml adsorbent dose, 300 rpm and 298k at different initial concentrations.

rotation the degree of aggregation of nano compounds adsorbent decrease which led to increasing the total adsorbent surface area and increasing the removal percentage of heavy metals. Therefore, rotation

leads to a decrease of the boundary layer and a decrease in the resistance of transportation of metal ions, this increases the transfer rate of the ions in solution [24].

Table 4. The variation of (ln k<sub>e</sub>) with a different temperature for solutions of (Zn<sup>2+</sup> and Ni<sup>2+</sup> at pH 6 and Fe<sup>3+</sup> at pH 7) adsorption on Nano bentonite (0.1g/200ml,300rpm) at equilibrium.

Nano bentonite	T (K)	298 K	303 K	308 K	313 K	323K
	1000/T	3.35	3.30	3.24	3.19	3.09
Fe <sup>3+</sup>	q <sub>e</sub>	180	182	184	186	190
	C <sub>e</sub>	8	7	6	5	3
	K <sub>e</sub>	22.5	26.0	30.6	37.2	63.3
	lnK <sub>e</sub>	3.1	3.2	3.4	3.6	4.1
Zn <sup>2+</sup>	q <sub>e</sub>	184	186	188	190	192
	C <sub>e</sub>	6	5	4	3	2
	K <sub>e</sub>	30.6	37.2	47.0	63.3	96.0
	lnK <sub>e</sub>	3.4	3.6	3.8	4.1	4.5
Ni <sup>2+</sup>	q <sub>e</sub>	182	184	188	192	194
	C <sub>e</sub>	7	6	4	2	1
	K <sub>e</sub>	26.0	30.6	47.0	96.0	194.0
	lnK <sub>e</sub>	3.2	3.4	3.8	4.5	5.2

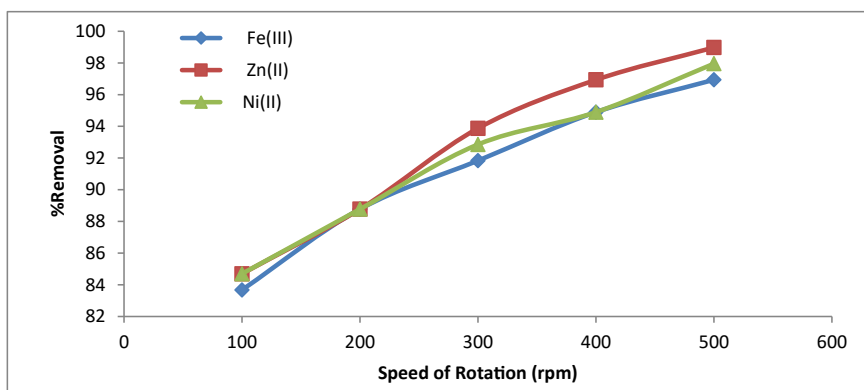


Figure 7. Speed of rotation effect on the %Removal of Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> on to Nano bentonite at constant pH, 0.1g/200 ml, C<sub>0</sub> = 100 mg/l, 298 K at time 120 min.

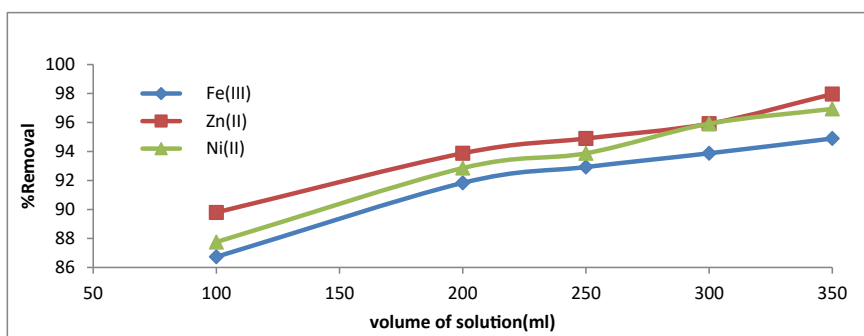


Figure 8. Effect of different volume of solution on %Removal of Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> on to Nano bentonite at constant pH, 0.1g/300 rpm, C<sub>0</sub> = 100 mg/l, 298 K at time 120 min.

3.7. Effect of volume

Figure 8 shows that the relationship between the different volume of solution on the rate of adsorption, by increasing Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> solution volume from 100 to 350 ml, Removal percentage increase so the relation between the quantity of adsorbed according to gram of adsorbent (q<sub>t</sub>) and volume of solution. It is clear that (q<sub>t</sub>) increases with increasing volume from 100 to 350 ml with Nano bentonite, that means at equilibrium (q<sub>e</sub>) increasing with volume increase at constant other parameters as shown in Figure 9 and this will be explained on the basis that there is an abundance of active sites on the surface of the adsorbent [25] that could adsorb more Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> by increasing its solution volume with Nano bentonite. Also maybe because the presence of nano compounds within the aqueous solution led to the aggregation of their particles and consequently decreasing the total surface area of the adsorbent.

3.8. Effect of pH

The influence of pH on the adsorption of Fe(III), Zn(II), and Ni(II) onto nano bentonite Examined at different values of pH 3,4,5,6 and 7 the other controlled parameters was kept at contact time 120 min to reach the complete equilibrium. The results show that adsorption percentage increased with increasing pH in the acid medium for Zn(II) and Ni(II) and give the highest value in pH = 6 then decrease due to the repulsion between adsorbent and Zn<sup>2+</sup> and Ni<sup>2+</sup>, this improving the adsorption capacity [26], and give the high adsorption in pH = 6 and (% Removal = 93.8 and 92.8) with Nano bentonite for Zn<sup>2+</sup> and Ni<sup>2+</sup> respectively. but For Iron The graph shows that the adsorption of on (Nano bentonite) surface increases in acid solution and arrive at pH = 7 give (% Removal = 91.9 %) and still increase that means that Fe(III) give high adsorption at alkaline media pH > 7 [27]. as shown in Figure 10.

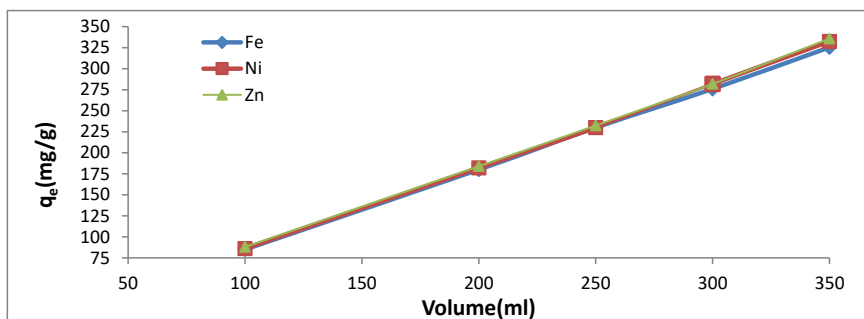


Figure 9. Effect of different volume of solution on the amount of metallic adsorbed (q<sub>e</sub>) of Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> on to Nano bentonite at constant pH, 0.1g/300rpm, C<sub>0</sub> 100 mg/l, 298 K at time 120 min.

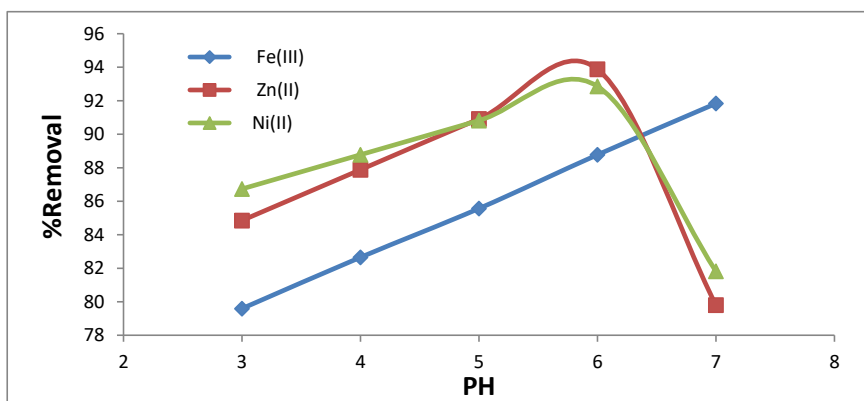


Figure 10. Effect of pH on the % removal of metal ions Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> (C<sub>0</sub> = 100 mg/l, 300 rpm, T = 298K, 0.1g/200ml Nano bentonite).

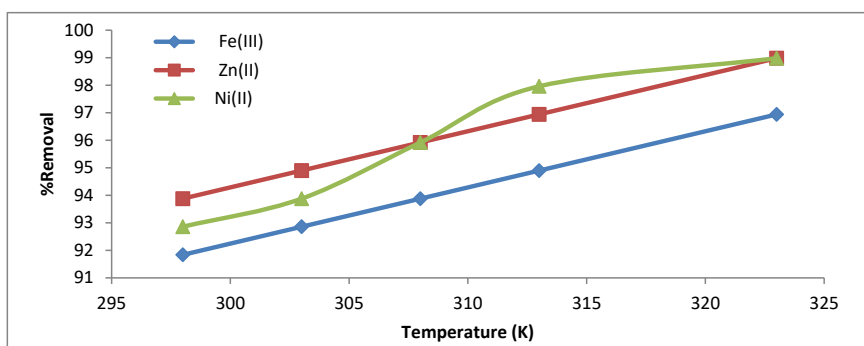


Figure 11. Contact time effect on the %Removal of Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> onto Nano bentonite at constant pH, 0.1g/200 ml, C<sub>0</sub> = 100 mg/l, 300 rpm at time 120 min and different temperatures.

### 3.9. Effect of temperature

The temperature of the solution has a significant effect on the adsorption capacity of the adsorbent. The adsorption experiments were conducted at different temperatures of 298K, 303K, 308K, 323K, and 323K. at a constant initial concentration of 100 mg/l, 300 rpm, and 0.1 g/200ml of Nano bentonite for Fe<sup>3+</sup> pH values >7, and for Zn<sup>2+</sup>, and Ni<sup>2+</sup> optimum pH 6, results show that the percentage of adsorption of Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> increases with increase in the temperature and give the highest value of adsorption at 323K, in the presence of Nano bentonite, as shown, Figure 11 %Removal increases from (91.8–96.9 %), (93.8–98.9 %) and (92.8–98.9 %) for Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> respectively. An increase in temperature involves increasing the mobility of metal ions and decreasing in the retarding forces acting on the diffusing ions; these result in the enhancement in the sportive capacity of the adsorbent, increasing the chemical interaction between adsorbate -adsorbent, and

creation of active surface centers or by an enhanced rate of intra-particle diffusion of Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> ions into the pores of the adsorbent at higher [28].

### 3.10. The thermodynamic parameters

The adsorption equilibrium data obtained at different temperatures were used to calculate the important thermodynamic parameters such as (Gibbs free energy (ΔG<sup>0</sup>), enthalpy change (ΔH<sup>0</sup>), and entropy change (ΔS<sup>0</sup>)) [29]. These parameters can be evaluated from the following equations:

$$\Delta G^0 = -RT \ln K_e \tag{6}$$

where, K<sub>e</sub> (l.g<sup>-1</sup>) and the equilibrium constant of adsorption calculated for each temperature from the equation:

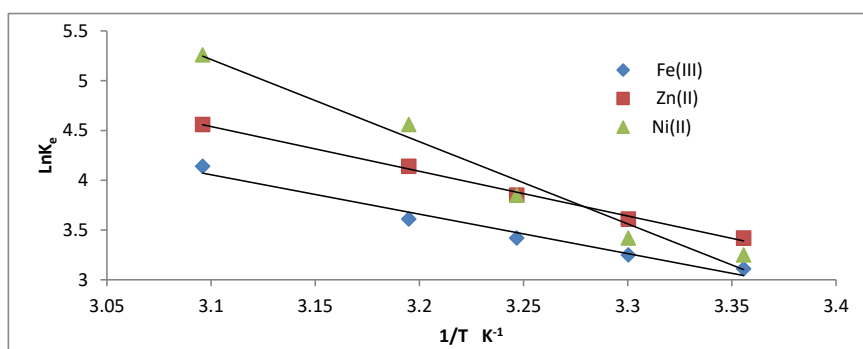
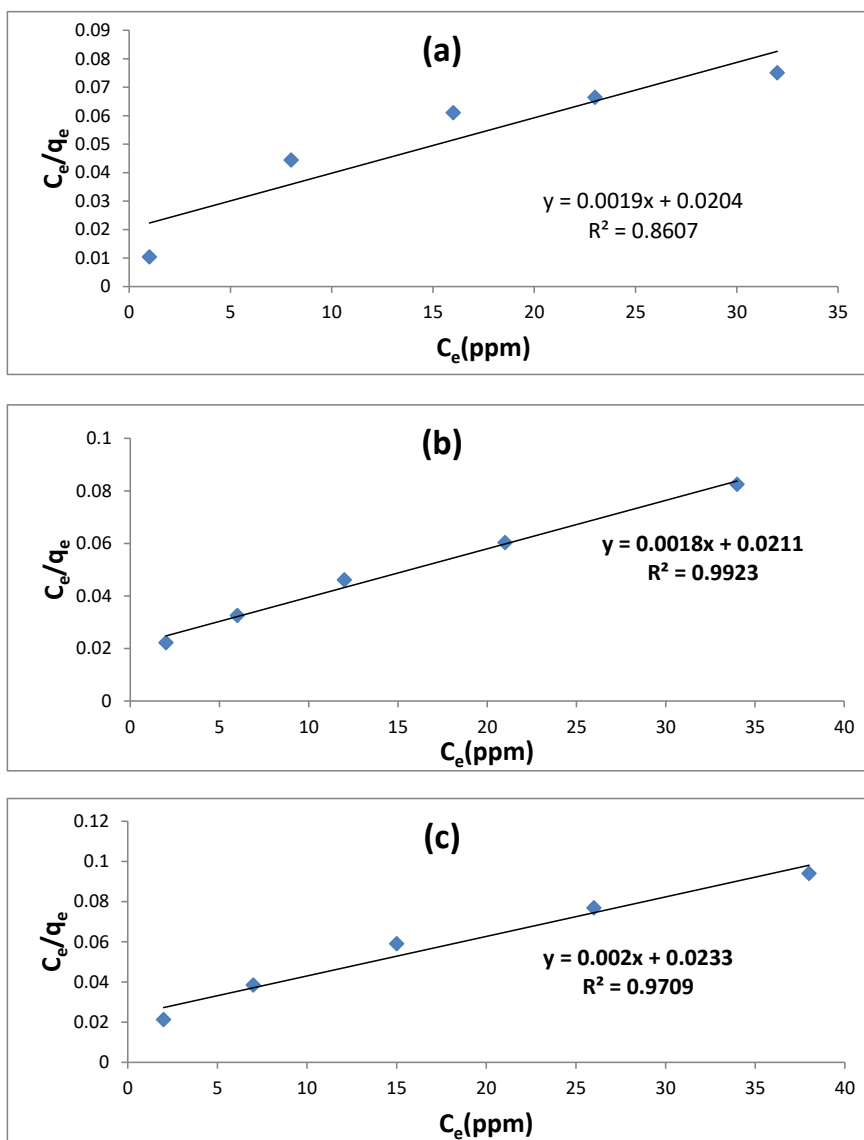


Figure 12. Relationship between ln K<sub>e</sub> and reciprocal of temperature for Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> adsorption on Nano bentonite, at optimum pH, C<sub>0</sub> of 100 mg l<sup>-1</sup>, dose 0.1g/200ml and 300 rpm.





**Figure 13.** The linear Langmuir adsorption isotherm for (a) Fe<sup>3+</sup>, (b) Zn<sup>2+</sup> and (c) Ni<sup>2+</sup> with nano bentonite at constant pH, 300 rpm, 298K, 0.1g/200ml and different initial concentration.

$$K_e = \frac{q_e}{C_e} \tag{7}$$

where  $q_e$  and  $c_e$  are the equilibrium concentrations for solute on the sorbent and in the solution, respectively.  $R$  (J/mol.K) is the gas constant 8.314 (J.mol<sup>-1</sup>.K<sup>-1</sup>),  $T$  (K) is the temperature absolute (Kelvin), the  $K_e$  (l.g<sup>-1</sup>) values are used in Equations (6) and (7) to determine ( $\Delta G^\circ$ ), ( $\Delta H^\circ$ ), and ( $\Delta S^\circ$ ) by the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

we can calculate the value of  $\ln K_e$  by the equation:

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

From equation [9] we can be calculated  $\Delta H^\circ$  and  $\Delta S^\circ$  values from the slope and intercept of Van't Hoff's plot of  $\ln(K_e)$  versus  $1/T$  these parameters as shown in Figure 12 for Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> adsorption on Nano bentonite and the values of ( $q_e$ ,  $c_e$ ,  $K_e$  and  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ ) were recorded in a Tables 4 and 5. The negative values of  $\Delta G^\circ$  confirm the feasibility of the process and the spontaneous nature of the adsorption of Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> adsorption on Nano bentonite. On the other hand, the more negative value with the increase in temperature indicates that better adsorption is obtained at higher temperatures. The positive values

**Table 5.** Thermodynamic parameters of Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> onto Nano bentonite at initial concentration of 100 mg/l.

Nano bentonite adsorbent	$\Delta H^\circ$ (K.jmol <sup>-1</sup> )	$\Delta S^\circ$ (Jmol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\circ$ (KJ.mol <sup>-1</sup> )				
			298K	303K	308K	313K	323K
Fe <sup>3+</sup>	32.93	135.8	-7705.42	-8052.1	-8473.29	-8944.03	-10257
Zn <sup>2+</sup>	37.4	153.8	-841.44	-9110	-9859.1	-10795.2	-12257.2
Ni <sup>2+</sup>	68.7	256.3	-8072.17	-8623.7	-9859.12	-11877.7	-14146.4

**Table 6.** Adsorption isotherm parameters for (a) Fe<sup>3+</sup>, (b) Zn<sup>2+</sup> and (c) Ni<sup>2+</sup> with nano bentonite at constant pH, 300 rpm, 298K, 0.5g/200ml and different initial concentration.

(a) Fe <sup>3+</sup>							
C <sub>o</sub> (mg/l)	Langmuir				Freundlich		
	R <sub>L</sub> (dm <sup>3</sup> /mg)	R <sup>2</sup> (mg/g)	q <sub>max</sub>	b	1/n	K <sub>f</sub>	R <sup>2</sup>
50	0.17	0.86	526.3	0.093	0.41	88.89	0.96
100	0.09						
150	0.06						
200	0.05						
250	0.04						
(b) Zn <sup>2+</sup>							
C <sub>o</sub> (mg/l)	Langmuir				Freundlich		
	R <sub>L</sub> (dm <sup>3</sup> /mg)	R <sup>2</sup> (mg/g)	q <sub>max</sub>	b	1/n	K <sub>f</sub>	R <sup>2</sup>
50	0.18	0.99	555.56	0.085	0.54	65.46	0.99
100	0.1						
150	0.07						
200	0.05						
250	0.04						
(c) Ni <sup>2+</sup>							
C <sub>o</sub> (mg/l)	Langmuir				Freundlich		
	R <sub>L</sub> (dm <sup>3</sup> /mg)	R <sup>2</sup> (mg/g)	q <sub>max</sub>	b	1/n	K <sub>f</sub>	R <sup>2</sup>
50	0.18	0.97	500	0.085	0.49	67.7	0.99
100	0.10						
150	0.07						
200	0.05						
250	0.04						

of ΔS° showed the increased randomness at solid/solution interfaces during the adsorption of metal ions onto adsorbent and also reflected the affinity of nano bentonite toward Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> ions under consideration, the positive value of enthalpy (ΔH°) indicated that the process had endothermic nature [30].

**3.11. Sorption isotherms**

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. Various isotherm equations are well known and two different isotherms are selected in this study, which is the Langmuir and Freundlich isotherms [31].

**3.11.1. Model of Langmuir isotherm**

Langmuir isotherm is primarily based at the monolayer sorption of Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> at surface of the adsorbent and is presented by:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \tag{10}$$

where, q<sub>e</sub> is the amount of metal ion at the adsorbent at equilibrium (mg/g), C<sub>e</sub> the concentration of metal ion inside the solution at equilibrium, q<sub>max</sub> the saturation capacity of monolayer adsorption at the adsorbent and (b) is the linear Langmuir constant [32]. By drawing relation of C<sub>e</sub>/q<sub>e</sub> Vs. C<sub>e</sub>. as shown in (Figure 13 a,b,c) for Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> we can be calculated the values of (q<sub>max</sub>) and (b) from the slope and intercept of the plots, respectively. R<sup>2</sup> values for metal ions detect the good application of the Langmuir model to these adsorptions, separation factor dimensionless constant (RL) which is defined as:

$$R_L = \frac{1}{1 + bC_o} \tag{11}$$

where C<sub>o</sub> is the initial metal ion concentration. The values of RL indicate the kind of isotherm is favorable, due to (0 < RL < 1) for all ions in the case of nano bentonite [33].

**3.11.2. Model of Freundlich isotherm**

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems [34]. The linearized form of the Freundlich isotherm equation is:

**Table 7.** The value of Fe<sup>3+</sup> ions concentration (mg/l) removed using different doses of Nano bentonite for wastewater sample and The relation between Nano bentonite dose and % removal for the wastewater sample.

Nano Bentonite Dose (g)	Fe <sup>3+</sup> ions concentration (mg/l)			%Removal		
	Sample (1)	Sample (2)	Sample (3)	Sample (1)	Sample (2)	Sample (3)
0.3	34	31	26	15.0	13.8	13.3
0.1	29	25	22	27.5	30.5	26.6
0.05	24	21	19	40.0	41.6	36.6
0.03	21	18	14	47.5	50.0	53.3
0.01	16	15	12	60.0	58.3	60.0

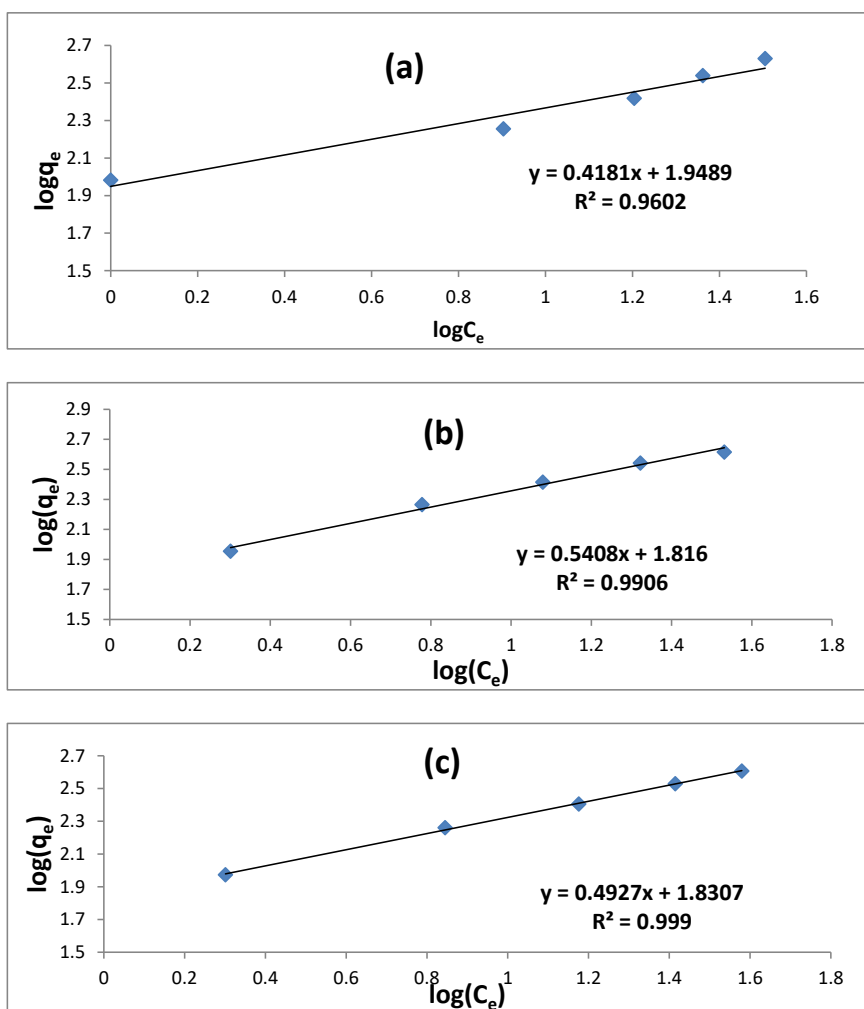


Figure 14. The linear Freundlich adsorption isotherm for (a) Fe<sup>3+</sup>, (b) Zn<sup>2+</sup> and (c) Ni<sup>2+</sup> with nano bentonite at constant pH, 300rpm, 298K, 0.1g/200ml and different initial concentration.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{12}$$

where the Freundlich constants  $KF$  and  $n$ , which respectively indicating the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope of the plot of  $\log q_e$  versus  $\log C_e$  for the adsorption of Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> ions onto nano bentonite as shown in

Figure 14 a, b,c. From the calculated data we can found that the Freundlich isotherm model fits very well than that of the Langmuir isotherm model when the  $R^2$  values are compared in Table 6. ( $R^2$  values of Freundlich plot  $>0.95$  were close to unity, indicating isotherm data fitted well to Freundlich model). The Freundlich constant  $n$  is the measure of the deviation from linearity of the adsorption. If a value for  $n$  is low than unity, this implies that the adsorption process is governed by a

Table 8. The value of Zn<sup>2+</sup> ions concentration (mg/l) removed using different doses of Nano bentonite for wastewater sample and The relation between Nano bentonite dose and % removal for the wastewater sample.

Nano Bentonite Dose (g)	Zn <sup>2+</sup> ions concentration (mg/l)			%Removal		
	Sample (1)	Sample (2)	Sample (3)	Sample (1)	Sample (2)	Sample (3)
0.3	47	42	36	6.0	8.6	10.0
0.1	37	33	27	26.0	28.2	32.5
0.05	28	23	18	44.0	50.0	55.0
0.03	21	16	12	58.0	65.2	70.0
0.01	16	11	8	68.0	76.0	80.0

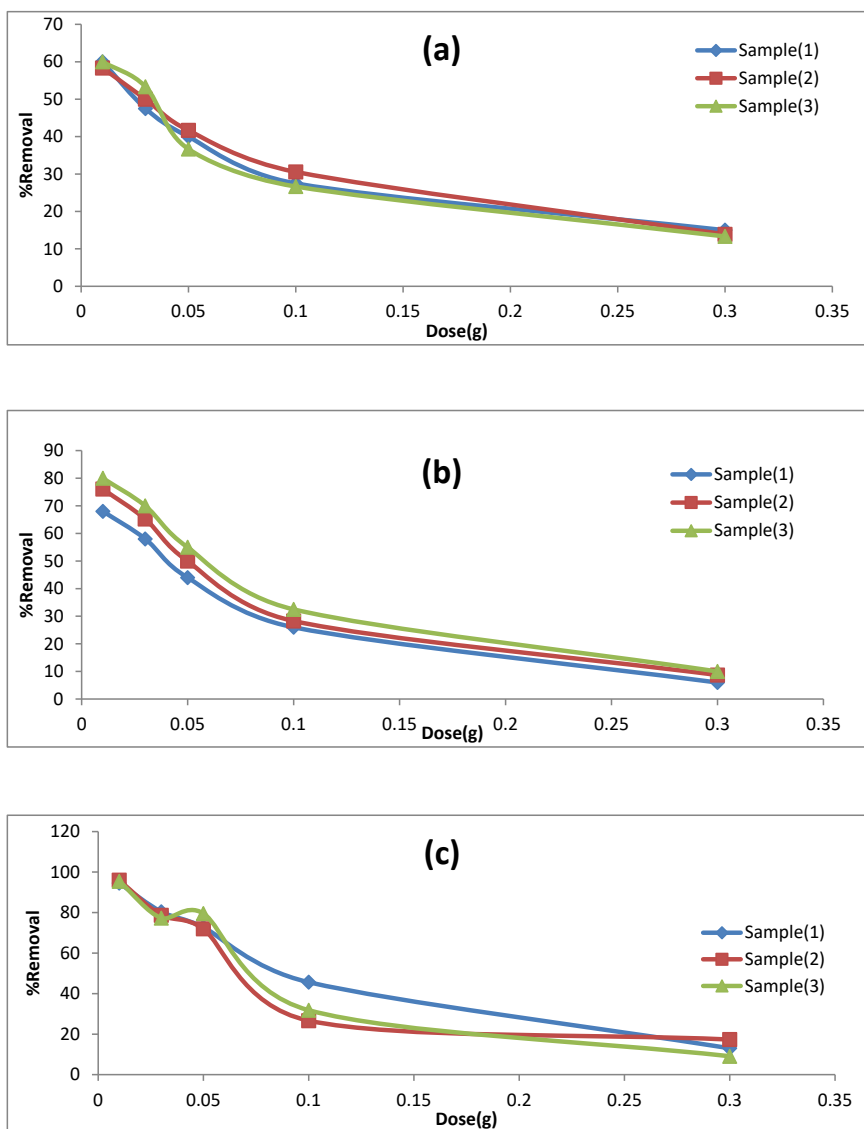


Figure 15. The relation between Nano bentonite dose and % removal for wastewater sample (a) Fe<sup>3+</sup>, (b) Zn<sup>2+</sup> and (c) Ni<sup>2+</sup>.

chemical mechanism, but a value for *n* is above unity, adsorption is favorable to a physical process. The values of *n* at equilibrium are (2.43, 1.85, and 1.49) for Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> respectively, representing favorable adsorption at studied temperatures and therefore this would seem to suggest that a physical mechanism, which is referred the adsorption bond weak and conducted with Van der Waals forces [35].

3.12. Application case

To demonstrate its practical application value, Nano bentonite was used to treat wastewater samples collected from the three different sources from the drainage of the electric power station, Damanhur, Egypt, which has an unknown concentration of iron ions, and other samples collected from one of the major metal coating workshops in

Table 9. The value of Ni<sup>2+</sup> ions concentration (mg/l) removed using different doses of Nano bentonite for wastewater sample and The relation between Nano bentonite dose and % removal for the wastewater sample.

Nano Bentonite Dose (g)	Ni <sup>2+</sup> ions concentration (mg/l)			%Removal		
	Sample (1)	Sample (2)	Sample (3)	Sample (1)	Sample (2)	Sample (3)
0.3	0.8	0.62	0.4	13.0	17.3	9.0
0.1	0.5	0.55	0.3	45.6	26.6	31.8
0.05	0.25	0.21	0.09	72.8	72.0	79.5
0.03	0.18	0.16	0.1	80.4	78.6	77.2
0.01	0.05	0.03	0.02	94.5	96.0	95.4

Almeria, Alexandria, Egypt, also from three different sources which have the unknown concentration of Zinc and Nickel ions.

#### Preparation of samples and procedure

- 1 Three drops of Conc.  $\text{HNO}_3$  per liter was added to the collected sample (to prevent metal precipitation).
- 2 The sample was then transferred to the laboratory where it was filter and pH was measured and found (7.8 and 9.5) for coating workshops and power station samples respectively.
- 3 After that pH was adjusted using (0.1N HCl and 0.1N NaOH) to be ( $7 > \text{pH} < 8$ ).

in the case of power station samples and pH adjusted to be ( $\text{pH} = 6$ ) in case of metal coating waste sample.

- 4 the aim of the experiment is studying the effect of different adsorbent dose of nano bentonite (0.01, 0.03, 0.05, 0.1, and 0.3 g) on all collected samples at fixed of other adsorption parameters (volume 200ml, speed of rotation 300rpm, pH, temperature 298K, and contact time 60min), after that, the reaction stopped, and the solution allowed to stele down then filtered, and the filtrate sample was measured using atomic absorption to know the concentration of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  ions.
- 5 In Tables 7, 8 and 9 we collecting the measurements results of collected samples concentration ions and after different doses of nano bentonite and calculated the %removal for each sample then drawing the relation between different doses of nano bentonite with the % removal of ions from wastewater as shown in (Figure 15 a,b,c) for iron, zinc, and Nickel respectively.

These results clearly show that Nano bentonite possesses potential application value. It can be noticed that the % removal of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  ions decreases with increasing nano bentonite dose from 0.01g to 0.3g that means that nano bentonite is effective in the elimination of toxic heavy metal ions from wastewater also with a low dose of nano sorbents can be arrived in good results of removing toxic metal ions from industrial wastewater [36].

## 4. Conclusion

The adsorption characteristics of nano bentonite were determined from adsorption studies using heavy metals such as Iron(III), zinc(II), and Nickel(II) as adsorbates. The important findings are summarized as, the % removal of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  ions increases with increasing temperature, speed of rotation, and volume of solution, but decreases with the increase in the adsorbent dose and initial concentration. The maximum % Removal of metal ions reached maximum value at  $\text{pH} = 6$  for ( $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ) and  $\text{pH} > 7$  for  $\text{Fe}^{3+}$  solution. Different thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  have been also evaluated and it has been found that the sorption was feasible, spontaneous, and endothermic. The positive value of the entropy change suggested the increased randomness. The correlation coefficient ( $R^2$ ) of the adsorption isotherm data showed that adsorption of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  ions on nano bentonite was better fitted to the Freundlich isotherm model. The pseudo-second-order kinetic order model is suitable for describing the adsorption system.

## Declarations

### Author contribution statement

A.M. Ahmed: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Mohamed I. Ayad and M. A. Darweesh: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Mohamed A Eledkawy: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Essam M. Elmelegy: Performed the experiments; Wrote the paper.

### Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

### Data availability statement

Data will be made available on request.

### Declaration of interests statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

## References

- [1] D. Frascari, G. Zanaroli, M.A. Motaleb, G. Annen, K. Belguith, S. Borin, C.V. Ortega, Integrated technological and management solutions for wastewater treatment and efficient agricultural reuse in Egypt, Morocco, and Tunisia, *Integrated Environ. Assess. Manag.* 14 (4) (2018) 447–462.
- [2] D. Pinelli, G. Zanaroli, A.A. Rashed, E. Oertlé, T. Wardenaar, M. Mancini, D. Frascari, Comparative preliminary evaluation of 2 in-stream water treatment technologies for the agricultural reuse of drainage water in the Nile Delta, *Integrated Environ. Assess. Manag.* 16 (6) (2020) 920–933.
- [3] H. Sadegh, G.A. Ali, V.K. Gupta, A.S.H. Makhoulf, R. Shahyari-ghoshehendi, M.N. Nadagouda, M. Sillanpää, E. Megiel, The role of a nanomaterial as effective adsorbents and their applications in wastewater treatment, *J. Nanostruct. Chem.* 7 (1) (2017) 1–14.
- [4] X. Liu, R. Ma, X. Wang, Y. Ma, Y. Yang, L. Zhuang, X. Wang, Graphene oxide-based materials for efficient removal of heavy metal ions from aqueous solution: a review, *Environ. Pollut.* 252 (2019) 62–73.
- [5] M. Sirait, P.D. Manalu, Preparation nature nano bentonite as adsorbent heavy metal Cd and Hg, *J. Phys. Conf.* 1120 (1) (2018).
- [6] N.P. Raval, P.U. Shah, N.K. Shah, Adsorptive removal of nickel (II) ions from the aqueous environment: a review, *J. Environ. Manag.* 179 (2016) 1–20.
- [7] M.B. Bazbouz, Preparation of Sodium-Activated Natural Bentonite Clay Incorporated Cellulose Acetate Nanofibres by Free Surface Electrospinning and its Proposed Applications. Chemistry Research and Applications, Nova Science Publishers, 2018.
- [8] H. Qu, S.Q. Liu, Removal of heavy metal ions from wastewater using modified sands: a brief review, in: *Key Engineering Materials*, Vol. 636, Trans Tech Publications Ltd, 2015, pp. 65–68.
- [9] R.M. Ali, H.A. Hamad, M.M. Hussein, G.F. Malash, Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism, and economic analysis, *Ecol. Eng.* 91 (2016) 317–332.
- [10] F. Shakerian, S. Dadfarnia, A.M.H. Shabani, M. Saeidi, S.M.S. Hosseini, Modified bentonite with dithizone as nano clay mineral adsorbent for solid-phase extraction of silver ions, *Croat. Chem. Acta* 89 (3) (2016) 309–317.
- [11] N. Banik, S.A. Jahan, S. Mostofa, H. Kabir, N. Sharmin, M. Rahman, S. Ahmed, Synthesis and characterization of organoclay modified with cetylpyridinium chloride, *Bangladesh J. Sci. Ind. Res.* 50 (1) (2015) 65–70.
- [12] C. Ponce, J.T. Kloprogge, Spectroscopic Studies of Synthetic and Natural Saponites: a Review, 2020, p. 2020110312. Preprints 2020.
- [13] K. Pramual, V. Intasanta, S. Chirachanchai, N. Chanlek, P. Kidkhunthod, A. Pongon, Urethane-linked imidazole-cellulose microcrystals: synthesis and their dual functions in adsorption and naked eye sensing with a colorimetric enhancement of metal ions, *ACS Sustain. Chem. Eng.* 6 (3) (2018) 3686–3695.
- [14] A. Abbas, A.M. Al-Amer, T. Laoui, M.J. Al-Marri, M.S. Nasser, M. Khraishah, M.A. Atieh, Heavy metal removal from aqueous solution by advanced carbon nanotubes: a critical review of adsorption applications, *Separ. Purif. Technol.* 157 (2016) 141–161.
- [15] P. Bartczak, Ł. Klapiszewski, M. Wysokowski, I. Majchrzak, W. Czernicka, A. Piasecki, T. Jesionowski, Treatment of model solutions and wastewater containing selected hazardous metal ions using a chitin/lignin hybrid material as an effective sorbent, *J. Environ. Manag.* 204 (2017) 300–310.

- [16] M. Shehata, S. El-Shafey, N.A. Ammar, A.M. El-Shamy, Reduction of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions from wastewater using mesoporous adsorbent: effect of treated wastewater on corrosion behavior of steel pipelines, Egypt. J. Chem. 62 (9) (2019) 1587–1602.
- [17] A.A. Adeyemo, I.O. Adeoye, O.S. Bello, Adsorption of dyes using different types of clay: a review, Appl. Water Sci. 7 (2) (2017) 543–568.
- [18] M.E. Batouti, A.M.M. Ahmed, N.A. Ibrahim, N. Mohamed, Adsorption of Co (II) on nano bentonite surface: kinetic and equilibrium study, Indian J. Chem. Technol. IJCT 24 (5) (2017) 461–470.
- [19] S. Rashid, C. Shen, J. Yang, J. Liu, J. Li, Preparation and properties of chitosan–metal complex: some factors influencing the adsorption capacity for dyes in aqueous solution, J. Environ. Sci. 66 (2018) 301–309.
- [20] N.H. Abdullah, K. Shameli, E.C. Abdullah, L.C. Abdullah, Solid matrices for the fabrication of magnetic iron oxide nanocomposites: synthesis, properties, and application for the adsorption of heavy metal ions and dyes, Compos. B Eng. 162 (2019) 538–568.
- [21] M.H. Dehghani, D. Sanaei, I. Ali, A. Bhatnagar, Removal of chromium (VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: kinetic modeling and isotherm studies, J. Mol. Liq. 215 (2016) 671–679.
- [22] Z.L. Chen, J.Q. Zhang, L. Huang, Z.H. Yuan, Z.J. Li, M.C. Liu, Removal of Cd and Pb with biochar made from dairy manure at low temperature, J. Integr. Agric. 18 (1) (2019) 201–210.
- [23] Y. Deng, S. Huang, D.A. Laird, X. Wang, Z. Meng, Adsorption behavior and mechanisms of cadmium and nickel on rice straw biochars in single-and binary-metal systems, Chemosphere 218 (2019) 308–318.
- [24] H. Piri-Moghadam, M.N. Alam, J. Pawliszyn, Review of geometries and coating materials in solid-phase microextraction: opportunities, limitations, and future perspectives, Anal. Chim. Acta 984 (2017) 42–65.
- [25] T.S. Anirudhan, J.R. Deepa, Synthesis and characterization of multi-carboxyl-functionalized nanocellulose/nano bentonite composite for the adsorption of uranium (VI) from aqueous solutions: kinetic and equilibrium profiles, Chem. Eng. J. 273 (2015) 390–400.
- [26] B. Hayati, A. Maleki, F. Najafi, H. Daraei, F. Gharibi, G. McKay, Synthesis and characterization of PAMAM/CNT nanocomposite as a super-capacity adsorbent for heavy metal ( $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Co}^{2+}$ ) removal from wastewater, J. Mol. Liq. 224 (2016) 1032–1040.
- [27] Z. Ajmal, A. Muhmood, M. Usman, S. Kizito, J. Lu, R. Dong, S. Wu, Phosphate removal from aqueous solution using iron oxides: adsorption, desorption, and regeneration characteristics, J. Colloid Interface Sci. 528 (2018) 145–155.
- [28] M. Yusuf, F.M. Elfghi, S.A. Zaidi, E.C. Abdullah, M.A. Khan, Applications of graphene and its derivatives as an adsorbent for heavy metal and dye removal: a systematic and comprehensive overview, RSC Adv. 5 (62) (2015) 50392–50420.
- [29] E.C. Lima, A. Hosseini-Bandegharaei, J.C. Moreno-Piraján, I. Anastopoulos, A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van't Hoof equation for calculation of thermodynamic parameters of adsorption, J. Mol. Liq. 273 (2019) 425–434.
- [30] E.C. Kaçakgil, D. Bingöl, Performance assessment and statistical modeling of modification and adsorptive properties of a lignocellulosic waste modified using reagent assisted mechanochemical process as a low-cost and high-performance method, Sustain. Chem. Pharm. 15 (2020) 100226.
- [31] N. Pradhan, E.R. Rene, P.N. Lens, L. Dipasquale, G. D'Ippolito, A. Fontana, G. Esposito, Adsorption behavior of lactic acid on granular activated carbon and anionic resins: thermodynamics, isotherms, and kinetic studies, Energies 10 (5) (2017) 665.
- [32] S.E. Abd Elhafez, H.A. Hamad, A.A. Zaatout, G.F. Malash, Management of agricultural waste for removal of heavy metals from aqueous solution: adsorption behaviors, adsorption mechanisms, environmental protection, and techno-economic analysis, Environ. Sci. Pollut. Control Ser. 24 (2) (2017) 1397–1415.
- [33] D. Balarak, F.K. Mostafapour, H. Azarpira, A. Joghataei, Langmuir, Freundlich, Temkin, and Dubinin–radushkevich isotherms studies of equilibrium sorption of ampicillin onto montmorillonite nanoparticles, J. Pharmaceut. Res. Int. (2017) 1–9.
- [34] K.C. Ng, M. Burhan, M.W. Shahzad, A.B. Ismail, A universal isotherm model to capture adsorption uptake and energy distribution of porous heterogeneous surface, Sci. Rep. 7 (1) (2017) 1–11.
- [35] M. Aden, J. Husson, S. Monney, M. Franchi, M. Knorr, M. Euvrard, Biosorption of Pb (II) ions from aqueous solution using alginates extracted from Djiboutian seaweeds and deposited on silica particles, Pure Appl. Chem. 91 (3) (2019) 459–475.
- [36] K. Atkowska, K. Lisichkov, G. Ruseska, A.T. Dimitrov, A. Grozdanov, Removal of heavy metal ions from wastewater using conventional and NanoSorbents: a review, J. Chem. Technol. Metall. 53 (2) (2018) .