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REMOVAL OF COPPER FROM INDUSTRIAL WASTEWATER USING MANGANESE FERRITE NANOPARTICLES: EVALUATION OF EQUILIBRIUM AND KINETIC MODEL

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Abstract

In this study, the removal of Cu(II) from real industrial wastewater, being taken from galvanotechnic industry, by means of manganese ferrite (MnFe_2O_4) nanoparticles (NPs) was investigated. The effects of pH, adsorbent dosage, and contact time on Cu(II) removal from wastewater were monitored using the real wastewater while the effect of initial concentration was studied on synthetic aqueous solutions. Optimal conditions were found for copper removal in this study. Cu(II) removal and adsorption capacity of MnFe_2O_4 NPs were achieved as 84.25% and 43.02 mg/g, respectively. In addition, other optimum conditions such as pH, adsorbent dosage and contact time were found as 5, 2 g/L and 120 min in this study, respectively. The removal of copper using MnFe_2O_4 NPs was fitted with Freundlich isotherm and pseudo second-order kinetic models. According to data obtained from desorption studies, MnFe_2O_4 NPs are regenerable and can be used several times. The results indicated that MnFe_2O_4 NPs are suitable adsorbents for removing Cu(II) from industrial wastewater.

Key words: adsorption, copper, manganese ferrite, nanoparticle, real wastewater treatment

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1. Introduction

Heavy metals are released into environment from many different industrial productions and various applications effluents such as battery, paint, metal coating, coal firing, domestic wastewater, vehicle emissions, the use of fossil fuels etc. (Ankit et al., 2011; Chen et al., 2010).

Metals, especially heavy metals, are known as the most critical contaminations, particularly in water and soil because of their toxicity for aquatic life as well as for animal, plant life and human health. Also, heavy metals are accumulated in receiving environment, plants or animals due to they are non-biodegradability (Ankit et al., 2011; Hoaghia et al., 2017; Mahdavi et al., 2013; Rahman and Islam, 2009). Copper is one of the important metal contaminants and it causes to considerable medical issues to people, for

example, stomach intestinal distress, kidney damage, anemia and even coma and eventual death (Kandah et al., 2003).

Due to negative effects of heavy metals on the aquatic environment and other living organisms their removal is important to control contamination in terms of economical elements. Nowadays, many different methods are used to remove heavy metals from aqueous solutions such as precipitation, filtration, reverse osmosis, adsorption, membrane separation, electrochemical methods and ion exchange in order to decrease the pollution impact of these metals (Atar et al., 2012; Osma et al., 2012; Predescu and Nicole, 2012). Of these techniques, adsorption is a standout amongst the most prescribed physicochemical treatment forms because of a portion of its qualities like high efficiency, easy operation, rapid response and low price (Chen et al., 2013; Omar et al., 2009).

There are many progressing researches on the utilization of adsorption strategies and adsorbents for heavy metal removal from wastewater, with the point of finding economical, widely applicable, and effective process that generates low amounts of sludge (Ahn et al., 2009; Rajic et al., 2010). Advantages and disadvantages of various different methods used to remove metals (especially heavy metals) from effluents are given in Table 1 (Ahmaruzzaman, 2009).

The sorbents or adsorbents to be applied in sorption techniques may contain natural or synthetic materials such as zeolites, clay, fly ash, bio sorbents, activated carbon, hydrogels and nanoparticles (Barakat, 2011; Mahdavi, 2013; Ren et al., 2013; Sezgin, 2012; Sezgin et al., 2016; Sezgin and Balkaya, 2017; Sharma et al., 2009; Srivastava et al., 2017; Wingenfelder et al., 2005). Nanomaterials such as carbon nanotubes, nanometal oxides, and magnetic nanoparticles have recently been investigated as available materials can be used for the heavy metals adsorption due to their special properties, such as a high adsorption capacity, unsaturated surfaces, easy operation, and easy production (Afkhami et al., 2010, 2011; Ahmadzadeh Tofighi and Mohammadi, 2011; Mahdavi et al., 2012; Meng et al., 2009; Ngomsik et al., 2005; Rahmani et al., 2010; Recillas et al., 2011; Zhang et al., 2008). Recently, nanoparticles have been suggested as efficient, low-cost, easy separation and environment friendly alternative to existing treatment materials compared to other adsorbent materials (Dimitrov, 2006; Dastjerdi and Montazer, 2010; Shan et al., 2009; Wang et al., 2011; Yang and Chen, 2005).

Copper (II) removal from real industrial wastewater was investigated in this study. For this aimed, manganese ferrite was synthesized as a novel nanoparticle using microwave-assisted combustion technique. This technique is easy and cheap method to

nanoparticles (NPs) synthesized as adsorbent of copper removal (Köseoglu, 2013a).

The adsorption behaviour of MnFe_2O_4 NPs were determined for Cu(II) removal under the multi (competitive) and single (non-competitive) conditions in this work. In addition, effects of parameters such as pH, dosage, initial concentrations and contact time on adsorption processes were investigated. After adsorption experiments desorption experiments were done in this study.

2. Experimental

2.1. Wastewater samples

Wastewater samples, which are used in this study, are taken from inflow of galvanotechnic industrial site (in Istanbul) wastewater treatment plant. Wastewater samples characterizations about cationic ions and wastewater pH are given Table 2.

2.2. MnFe_2O_4 NPs synthesis

All the chemicals used for the synthesis of NPs were analytically pure and received from Merck Chemicals Company, and they were used as received without further purification. Nanocrystalline MnFe_2O_4 powders were synthesized through a microwave-assisted combustion synthesis process as previously described in the literature (Köseoglu, 2013a, 2013b; Sertkol et al., 2009, 2010). Stoichiometric amounts of manganese nitrate, iron nitrate and urea were dissolved in deionized water. The solutions are poured into a crucible and placed in a microwave-oven.

After boiling and dehydration, the solution reached the point of spontaneous combustion. Finally, the solution burns and releases lots of heat and becomes solid.

Table 1. Comparisons of different methods used for heavy metals removal from wastewater (Ahmaruzzaman, 2009)

<i>Physical and /or chemical methods</i>	<i>Advantages</i>	<i>Disadvantages</i>
Oxidation	Quick process for the removal toxic contaminant	High costs and generation of by-products
Ion exchange	Good removal of an extended range of metals	Absorbent requires regeneration or disposal
Membrane filtration technologies	Good for heavy metals removal	Concentrated sludge production and high energy costs
Adsorption	Designation of process is simple and flexible, operation procedures are easy and for toxic pollutants sensitivity is none	Adsorbents requires regeneration
Coagulation/flocculation	Economically feasible	High sludge production and generation of large particles
Electrochemical treatment	Quick process and effective for defined metal ions	High costs and generation of by-products
Ozonation	Applied in gaseous state: alteration of volume	Short half life
Photochemical	Sludge generation is none	Generation of by-products
Irradiation	Effective at lab scale	Required a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production
Fentons reagents	Effective and capable of treating variety of wastes and no energy input required to activate hydrogen peroxide	Sludge production
Biological treatment	Feasible in removing some metals	Technology yet to be established and commercialized

A Huber JSO-DEBYEFLEX 1001 diffractometer was used to carry out the X-ray powder diffraction analysis in order to characterize the product. Additional, by using NOVA3200 E analytical system, the specific surface area of NPs was measured and Burnauer-Emmett-Teller (BET) N₂ method was used to calculate the specific surface area of NPs.

Table 2. Cationic ions concentrations and pH value of industrial wastewater

Cations	Concentration (mg/L)
Cu ⁺²	86.12
Ni ⁺²	83.99
Zn ⁺²	178.30
Total Cr	302.80
Total Fe	77.74
Na ⁺	822.88
NH ₄ ⁺	181.23
K ⁺	146.81
Mg ⁺²	59.01
Ca ⁺²	212.22
pH = 2	

2.3 Experimental procedures

All the copper adsorption experiments were conducted at 25 °C. Prior to experiments; the wastewater was filtered with a mesh size of 0.45 µm. For batch tests, the adsorbent (MnFe₂O₄ NPs) was added to 20 mL of the synthetic and industrial wastewater samples placed in 100 mL Erlenmeyer flasks; than shaken at 150 rpm in a Gallenkamp orbital incubator. The samples were filtered with a mesh size of 0.22 µm and then transferred to glass tubes for analysis. Before and after adsorption, atomic absorption spectroscopy (Perkin-Elmer Analyst 400) was used the Cu(II) concentrations of the solutions.

The copper removal efficiency and adsorption capacity of NPs were calculated by using Eq. (1) and Eq. (2) respectively.

$$\text{Removal Efficiency} = \frac{(C_0 - C_e)}{C_0} * 100 \quad (1)$$

$$q = \frac{(C_0 - C_e)}{m} * V \quad (2)$$

where, C_0 is copper initial concentration in the wastewater (mg/L); C_e is the residual concentrations of copper in the solution (mg/L); q represents adsorption capacity in the equilibrium conditions (mg/g); V is the sample volume (L) and m is amount of manganese ferrite NPs used in the experiment (g).

Various experiments were carried out to evaluate the effects of pH, initial copper concentrations, contact time and NPs dosages on copper adsorption. For this purpose, experiments were carried out at various pH values (2.0-7.0, with adding NaOH or HCl prior to the experiments), adsorbent dosage (0.5, 1.0, 1.5, 2.0, 4.0, and 6.0 g/L), contact times (10–1440 min.) and initial metal concentrations (15–450 mg/L) in the wastewater (real and synthetic)

samples. After the Cu(II) adsorption by MnFe₂O₄ NPs desorption study was conducted. Cu(II) loaded nanoparticles were resuspended in 50 mL of 0.01 M HCl and this suspension was shaken for 20 minutes at room temperature. Afterwards, MnFe₂O₄ NPs were separated by external magnetic field and washed with distilled water until neutralization and finally dried for reusing. The adsorption process was repeated using the regenerated MnFe₂O₄ NPs.

2.4. Theory

2.4.1. Adsorption isotherm

Adsorption models of Langmuir, Freundlich, and Temkin were used for determining adsorption isotherm in this study. These models are commonly used in adsorption processes. The linear Langmuir isotherm form is given below (Langmuir, 1908) (Eq. 3):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

where, C_e represents the residual concentration of adsorbate in the equilibrium conditions (mg/L); q_e represents the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g); q_m represents the calculating theoretical adsorbent maximum adsorption capacity as monolayer (mg/g); K_L represents the Langmuir isotherm constant which is concerned to the adsorption energy (L/mg), the relationship between the adsorbent and the adsorbate. The q_m and K_L values are determined from the slope and intercept of the linear plot of C_e/q_e versus C_e .

The linear Freundlich isotherm form is expressed as follows (Freundlich, 1906) (Eq. 4):

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

where, K_f represents the Freundlich isotherm constant which is relationship the adsorption capacity of the adsorbent (mg/g), and $1/n$ represents the adsorption intensity that ranges between 0 and 1, where zero represents maximum heterogeneity of adsorbent surface. $1/n$ represents favorability of the adsorption. K_f and $1/n$ The values were found from the intercept and the slope of the $\ln q_e$ versus $\ln C_e$ plot.

In addition, the Temkin isotherm includes a factor that clearly takes into account the adsorbing species-adsorbate interactions; the isotherm is given by a linearized expression as (Temkin and Pyzhev, 1940) (Eq. 5):

$$q_e = B_T \ln K_t + B_T \ln C_e \quad (5)$$

where, $B_T = RT/b$ (R is the universal gas constant (8.314 J/mol-K), T represents temperature (K), b is the constant of Temkin dependent on adsorption energy (kJ/mol) and K_T represents the binding constant at equilibrium which is related to the maximum binding

energy (L/mg). The K_T and B_T values were calculated from the intercept and slope of the q_e versus $\ln C_e$ plot.

2.4.2. Adsorption kinetics

Pseudo (first-order and second-order) kinetic models equations developed by Lagergren (1898) are generally used as the kinetic model to determine reaction degrees of adsorption systems (Baral et al., 2009; Ho and McKay, 1999; Zhao et al., 2011). The equation of pseudo first-order kinetic model (linear form) is expressed as follows (Lagergren, 1898; Singh et al., 2005) (Eq. 6):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where, q_e and q_t are the adsorption amounts of heavy metal ions per gram of adsorbent material time t (min) and at equilibrium conditions, respectively (mg/g); k_1 is the pseudo-first-order adsorption rate constant (min^{-1}); t is time (min). The adsorption rate constant k_1 and equilibrium adsorption capacity q_e , calculated from the slopes and intercepts of plots of $\log(q_e - q_t)$ versus t .

The equation of the pseudo second-order kinetic model (linear form) is as follows (Lagergren, 1898; Singh et al., 2005) (Eq.7):

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \quad (7)$$

where k_2 is the equilibrium rate constant for pseudo-second-order adsorption ($\text{g.mg}^{-1}.\text{min}^{-1}$). The adsorption rate constant k_2 and equilibrium adsorption capacity q_e , calculated from the slopes and intercepts of plots of t/q_t versus t .

When q_e values calculated using experimental data correlate with theoretical values and according to correlation coefficient (R^2) values, adsorption rate is deemed to fit the pseudo first or second-order kinetic models. The adsorption data were subject to piecewise linear regression analysis to understand the mechanism of adsorption. On the other hand, intraparticle diffusion model developed by Weber–Morris has commonly been used to optimize the design of adsorbents and adsorption conditions (Boparai et al., 2011). This model and using other kinetic models (Pseudo first-order and pseudo second-order model) can be obtained the information about adsorption mechanism (Chingombe et al., 2006; Ozcan et al., 2007; Unuabonah et al., 2007; Wu et al., 2009). Also, the rate limiting step can be determined by using intraparticle diffusion model that is given follow equation (Taqvi et al., 2007; Kavitha and Namasivayam, 2007) (Eq. 8):

$$q_t = k_i t^{0.5} + C \quad (8)$$

where, k_i is the constant of intraparticle diffusion rate ($\text{mg.g}^{-1}.\text{min}^{0.5}$) and C is the intercept. According to this model, a plot of q_t versus $t^{0.5}$ should be linear if intraparticle diffusion is involved in the adsorption process and if the plot passes through the origin then

intraparticle diffusion is the sole rate-limiting step (Ozcan et al., 2007). It has also been suggested that in instances when q_t versus $t^{0.5}$ is multi linear, two or more steps govern the adsorption process (Unuabonah et al., 2007; Wu et al., 2009).

3. Results and discussion

3.1. Characterization of MnFe_2O_4 NPs

X-ray diffraction (XRD) was used for the phase composition determining of synthesized manganese ferrite NPs and XRD pattern is given in Fig. 1. As seen in Fig. 1 synthesized manganese ferrite NPs sample has a single spinel phase with good crystallinity. In comparison of the XRD patterns of present investigations with the standard data (JCPDS file no: 74-2403 for MnFe_2O_4) (Günay et al. 2013, Köseoğlu et al. 2012), it has been concluded that sample is indexed perfectly to the cubic spinel MnFe_2O_4 structure indicated in the reflecting planes with the hkl values of (111), (220), (311), (222), (400), (422), (511), (440) in XRD powder pattern. In addition, the product has a specific surface area of $28.95 \text{ m}^2.\text{g}^{-1}$, as measured by BET.

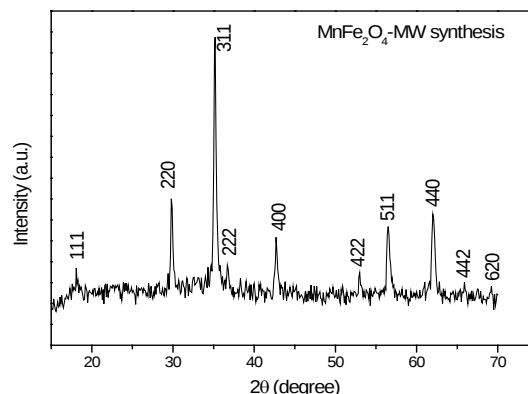


Fig. 1. XRD pattern of MnFe_2O_4 NPs

3.1. pH effect

Fig. 2 shows the pH effect on Cu(II) adsorption by MnFe_2O_4 NPs. As can be seen, the removal efficiency and adsorption capacity of Cu(II) tended to increase with increasing pH value. According to Fig. 2, the removal efficiency and adsorption capacity of Cu(II) was very less (3.43% and 0.88 mg/g) at an initial pH value of 2.0. A sharp increase in the adsorption of copper occurred in the pH range of 3.0–5.0 and the removal efficiency and adsorption capacity of Cu(II) reached 91.56% and 23.37 mg/g, respectively. It was observed that the adsorption capacity was very low at strong acidic medium and the adsorption capacity increases with increasing pH values. This may be elucidated on the principles of decrease in competition between positively charged H^+ , H_3O^+ and Cu^{2+} for the same functional groups. As the pH value was increased, more ligands were exposed and the number of negatively charged groups

on the adsorbent matrix probably increased, enhancing the removal cationic species (Reddad et al., 2002). Fig. 2 shows that the maximum removal and adsorption capacity were found at pH 7. It was also observed that Cu(II) removal and the adsorption capacity were increased again at pH value from 6.0 to 7.0, which might be due to the onset of precipitation of copper ions as insoluble $\text{Cu}(\text{OH})_2$ and not because of the adsorption (Rahman and Islam, 2009; Rashidi et al., 2010). However, a pH value of 5.0 was chosen as being the optimum for further experiment to avoid the precipitation of $\text{Cu}(\text{OH})^{2+}$ as Cu^{2+} precipitates above pH 6.5 in the form of $\text{Cu}(\text{OH})_2$ (Rahman, 2007).

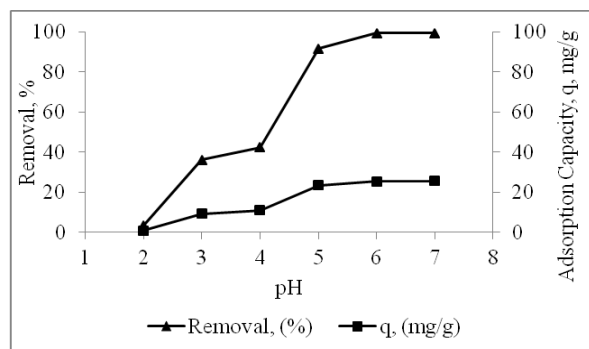


Fig. 2. pH effect on copper adsorption (Conditions: NPs dosage= 4 g/L, time= 1440 min., speed= 150 rpm)

3.2. MnFe_2O_4 NPs dosage effect

The effect of MnFe_2O_4 dosage on Cu(II) removal is shown in Fig. 3. As can be seen, the removal of Cu(II) was increased with the increase in adsorbent dosage. As the adsorbent dosage increases, surface area of the adsorbent increases as well. At higher adsorbent dosage, the equilibrium time will be shorter since more adsorption sites will be available to remove copper from the aqueous solution (Garg et al., 2004). However, adsorption capacities decreased from 144.52 mg/g to 13.97 mg/g while adsorbent dosage increased from 0.5 to 6.0 g/L. According to Garg et al. (2004), this can be given to aggregation and/or overlapping of adsorbent surface area available for copper removal and increase in diffusion path length. Beyond the certain amount (2 g), the Cu(II) removal percentage reaches almost a constant value. The removal efficiency and adsorption capacity of Cu(II) in the presence of 2 g/L MnFe_2O_4 NPs were 84.25% and 43.02 mg/g, respectively. This value is higher than adsorption capacities of various adsorbents as activated carbon being modified by poly(N,N-dimethylaminoethyl methacrylate) (31.46 mg/g) (Zhu et al., 2009), carbon nanotube (24.49 mg/g) (Rao et al., 2007), oxidized and unmodified coir (6.99 and 2.54 mg/g) (Shukla et al., 2009), sepiolite (38.17 mg/g) (Dogan et al., 2009), copper ferrite and nickel ferrite NPs (3.95 and 4.38 mg/g) (Sezgin et al., 2013) and amino-functionalized magnetic nanosorbent (25.77) (Yong-Mei et al., 2010). In addition, Cu(II) adsorption

capacity of MnFe_2O_4 NPs was found close to some magnetic nanoparticle adsorbent due to the magnetic gamma- Fe_2O_3 nanoparticles coated with poly-L-cysteine (42.9 mg/g) (White et al., 2009), and Fe_3O_4 magnetic nanoparticles coated with humic acid (46.3 mg/g) (Liu et al., 2008). According to these results, MnFe_2O_4 NPs are better than some natural or modified adsorbent for the removal of copper.

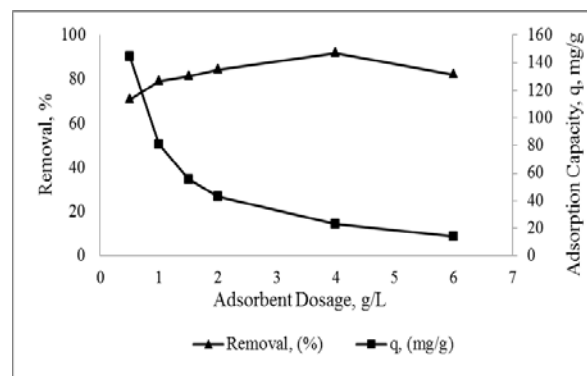


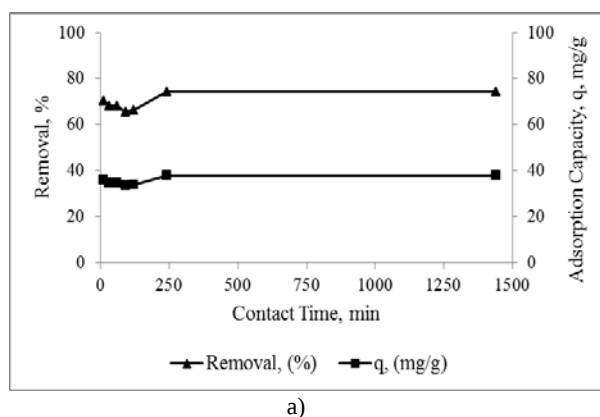
Fig. 3. NPs dosage Effect on copper adsorption (Conditions: pH= 5, time= 1440 min., speed= 150 rpm)

3.3. Contact time effect

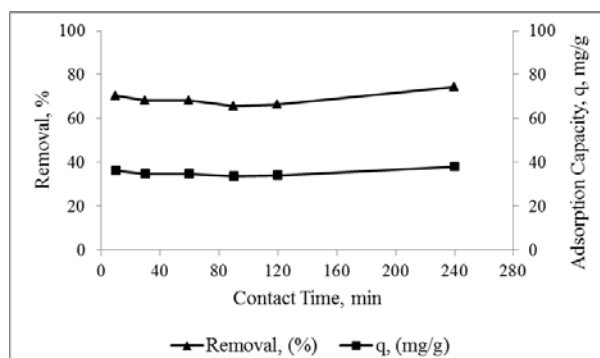
Contact time is significant to determine the adsorption kinetics and feasibility of the system in practice (Chen and Wang, 2009; Xu et al., 2011). The contact time effect on Cu(II) removal is presented in Fig. 4 (a and b). Accordingly, no significant increase or decrease was found in Cu(II) removal and adsorption capacities was found between 10 and 120 min, thereafter these capacities increased slowly (Fig. 4b detailed figure for 10 and 240 min). According to the results, the equilibrium condition is reached at 120 min and it was taken as optimal contact time for the subsequent experiments.

3.4. Initial Cu(II) concentrations effect

The results of removal of Cu(II) for different initial concentrations, which were prepared from synthetic solutions, are presented in Fig. 5. Fig. 5 shows that no significant change occurred for percentage removal of Cu(II). However, the Cu(II) quantity adsorbed per unit amount of adsorbent increased with increasing initial Cu(II) concentrations. The initial concentration ensures a significant impellent power to overcome all mass transfer resistance of Cu(II) ions between the aqueous and solid phases, hence a higher initial concentration of Cu(II) ions may increase the adsorption capacity. Ozer et al., (2004) indicated that all available Cu(II) ions in solution could interact with the binding sites at lower concentrations and thus the percentage adsorption was higher than those at higher initial Cu(II) ion concentrations. At higher concentrations, lower adsorption yield results from the saturation of adsorption sites.



a)



b)

Fig. 4. a) Contact time effect on copper adsorption, b) detail figure for 10 and 240 min (Conditions: NPs dosage= 2 g/L, pH= 5, speed= 150 rpm)

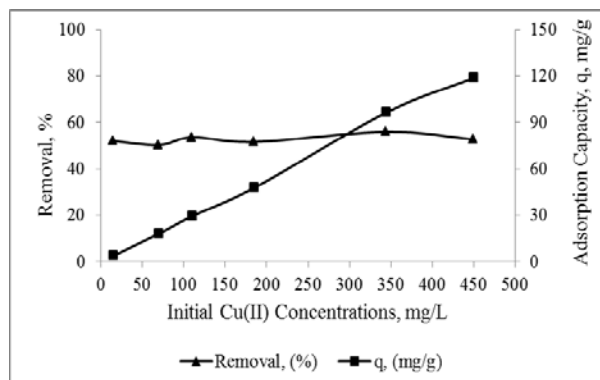


Fig. 5. Initial concentrations effect on copper adsorption (Conditions: NPs dosage= 2 g/L, pH= 5, time= 120 min, speed= 150 rpm)

3.5. Adsorption isotherms

The adsorption data were applied to the Langmuir, Freundlich, and the Temkin equations. The coefficients for the linearized forms of the Langmuir, Freundlich, and Temkin isotherms were found as 0.841, 0.998, and 0.796 respectively. Thus, Cu(II) adsorption is better fitted to the Freundlich model. Accordingly, it is assumed that adsorption sites on the adsorbent surface are heterogeneous and there was no interaction between the molecules adsorbed onto the surface (Ng et al., 2003). Furthermore, K_f and n values

in the Freundlich isotherm, parameters and isotherm plot of which are given in Table 3 and Fig. 6, respectively, give information about the suitability of adsorbent/adsorbate system and adsorption system (Anirudhan and Suchithra, 2010; Donat et al., 2005; Monser and Adhoum, 2002). If $n < 1$, the adsorption system is more heterogeneous, and the adsorption is more efficient at high concentrations. If n is equal to unity, the adsorption is linear. When $n > 1$, this indicates that the system is more efficient at low concentrations (Anirudhan and Suchithra, 2010; Babel and Kurniawan, 2004; Balkaya and Cesur, 2008; Donat et al., 2005).

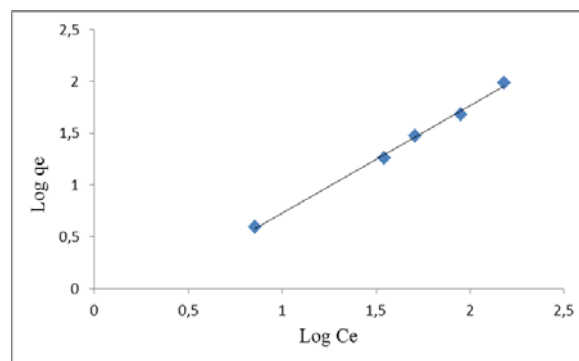


Fig. 6. The graph of Freundlich isotherm for the adsorption of Cu(II) on MnFe₂O₄ NPs

3.6. Adsorption kinetics

The pseudo kinetics models (first-order and second order) were conducted to explain adsorption mechanisms in Cu(II) removal with MnFe₂O₄ NPs. The values of the parameters and R^2 are given in Table 4. As can be seen in Table 4, the correlation coefficient calculated from the pseudo-second-order model were high (0.994) for Cu(II) removal, and the calculated q_e values from this model were in well agreement with the q_e values of experimental. Thus, according to the results of kinetic models were given in Table 4, the Cu(II) adsorption of MnFe₂O₄ NPs tracked a pseudo second-order kinetic model. A plot of pseudo-second-order adsorption kinetic model is shown in Fig. 7.

Intraparticle diffusion plot q_t vs $t^{0.5}$ was given in Fig. 8. According to Fig. 8, the adsorption Cu(II) on MnFe₂O₄ NPs occurred in two phases. The initial linear section represents a gradual adsorption stage where intraparticle or pore diffusion is rate limiting and the second section plot is final equilibrium stage.

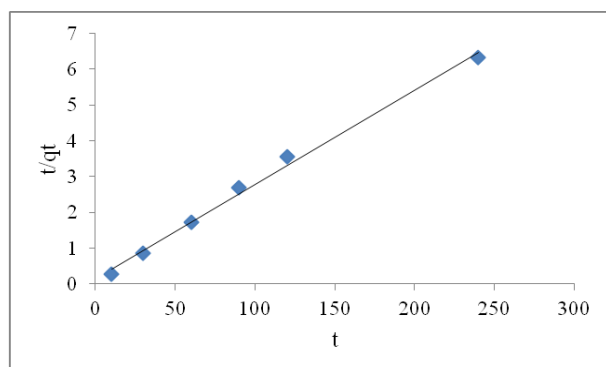
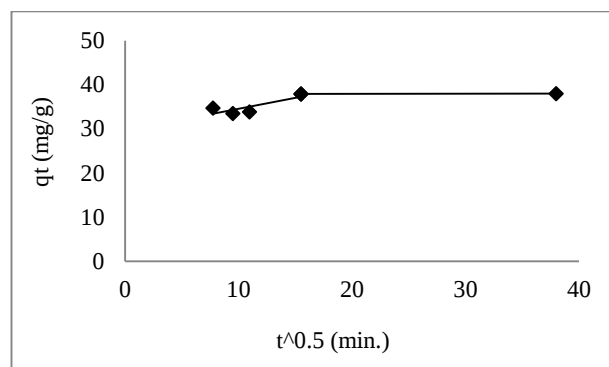
Because of the intraparticle diffusion line that was given in Fig. 8 did not pass through the origin, this diffusion was not the only rate limiting step on the adsorption process. So that, multiple diffusion model was determined to be effective in adsorption. In addition, the intraparticle diffusion rate k_i and plot intercept value C were found 0.49 mg g⁻¹ min^{0.5} and 29.63, respectively. According to the results of kinetic study, it can also be suggested that the adsorption mechanism is controlled by chemical adsorption.

Table 3. Langmuir, Freundlich and Temkin isotherm parameters

	<i>Langmuir</i>			<i>Freundlich</i>			<i>Temkin</i>		
	q_m (mg/g)	K (L/mg)	R^2	K_f (mg/g)	n	R^2	K_T (L/mg)	b	R^2
Cu(II)	434.78	0.001	0.841	0.486	0.963	0.998	0.083	74.167	0.796

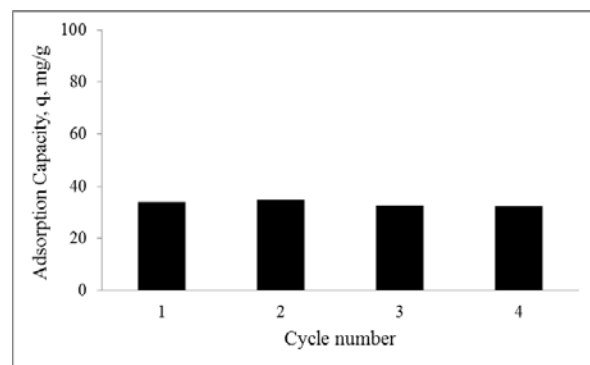
Table 4. Kinetic parameters for the Cu(II) adsorption

<i>Pseudo first-order</i>				<i>Pseudo second-order</i>			
R^2	k_1	$q_{e,cal}$	$q_{e,exp}$	R^2	k_2	$q_{e,cal}$	$q_{e,exp}$
0.761	0.0059	2.32	38.05	0.994	0.0045	38.02	38.05

**Fig. 7.** A plot of t/q vs. time according to pseudo-second-order adsorption kinetics**Fig. 8.** Intraparticle diffusion plot for Cu(II) adsorption on MnFe₂O₄ NPs

3.7. Desorption

Fig. 9 shows that adsorption capacities of MnFe₂O₄ NPs undergo through four cycles.

**Fig. 9.** Cu(II) adsorption capacities of the regenerated MnFe₂O₄ NPs

According to Fig. 9, there is no change in Cu(II) adsorption capacity of MnFe₂O₄ NPs after four cycles. In the desorption studies, it has been determined that MnFe₂O₄ NPs are regenerable and can be used several times.

4. Conclusions

For the copper (II) removal from an industrial wastewater (galvanotechnic industry) using adsorption method, MnFe₂O₄ nanoparticles were synthesized as a novel adsorbent that was ensured owing to an effective, rapid, reasonably priced and applicable method in this study. Microwave-assisted combustion process was used a simple synthesis

method for NPs. The equilibrium of adsorption process was reached in 120 min, and maximum Cu (II) ions adsorption were obtained at pH 5. It is no significant effect that increasing initial copper concentrations on Cu(II) adsorption using manganese ferrite NPs. The most suitable as a kinetic model was determined the pseudo-second-order model and intraparticle diffusion was not the only rate limiting step on the adsorption process. The Freundlich isotherm model could be well fitting model according to isotherm analysis data presented in this study. In additional, the desorption studies showed that the MnFe₂O₄ NPs have a high stability and good reusability in this study and they have a great potential in practical application.

Consequently, this study showed that MnFe₂O₄ NPs, as a novel adsorbent, would be useful, highly effective, economic and reusable for Cu(II) removal from industrial wastewater, by means of reducing the problems associated with treating sludge derived from chemical precipitation processes.

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