Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2017.21385

88 (2017) 145–153
September

Studies on natural biogenic iron oxides for removal of copper (II) ion from aqueous solution

Brij Kishor, Nekram Rawal*

Department of Civil Engineering, MNNIT Allahabad-211004, India, email: brijkishorgood@gmail.com (B. Kishor), nek_friend@rediffmail.com (N. Rawal)

Received 25 February 2017; Accepted 26 August 2017

ABSTRACT

In the past few decades, presence of heavy metals such as copper has increased in the environment due to its industrial applications. Therefore, it is important to remove copper metal ions from water and wastewater so as to restrict it upto desired limits. This can be achieved by cost effective adsorption method on natural biogenic iron oxides as an adsorbent. Both forms of natural biogenic iron oxides i.e. banded iron formation (BIF) and iron plaque of *Typha-latifolia* have been characterized by environmental scanning electron microscopy (ESEM) and energy-dispersive X-ray spectroscopy (EDX). In the present study, the influence of adsorbent dose, the initial Cu(II) concentration and contact time for the removal of Cu(II) from aqueous solution has been ascertained. The present study reveals that BIF form of natural biogenic iron oxide showed higher removal potential compared to iron plaque particle of *Typha-latifolia*. The maximum sorption efficiency was found to be 88.65% at 30 g/L adsorbent dose. The Freundlich isotherm best fitted with (R^2) value of 0.999 are compared with Langmuir and Redlich-Peterson adsorption isotherms. The Pseudo first order kinetics rate reaction has been fitted to describe the batch kinetics of the Cu(II) uptake by BIF.

Keywords: Adsorption; Copper (II); Banded iron formation (BIF); Iron plaque of *Typha-latifolia*

1. Introduction

The heavy metals released into nature have posed significant threat to public health and environment because of their toxicity and long-term persistent in nature. The toxic heavy metals in wastewaters and surface waters are a worldwide problem for the environmental engineers [1]. Copper is one of the important and oldest heavy metal used since the development of civilization. Copper is an important material for the industrial development as well as an essential element for metabolism activity. Copper (II) ion was released into water bodies through industries including manufacturing of printed circuit board, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives, mining and smelting, brass manufacturing, electroplating, and petroleum refining etc. [2]. Copper (II) ion has toxic effect on human beings as well as on ecosystem due to non-biodegradability, biomagnification and long term persistent in the environment [3]. The copper (II) ion intake beyond the limits by human beings leads to health hazards like mucosal irritation, capillary damage, hepatic damage, renal damage. Excessive amount of copper (II) ion in the human body causes severe hemolysis, hepatotoxic and nephrotoxic effects like vomiting, depression, gastrointestinal irritation, cramps, central nervous system problems, convulsions or even death [4]. Therefore, it need to be removed from water and wastewater for protecting public health and environment. Removal of Cu(II) ions from water and wastewater is achieved by chemical precipitation, coagulation, solvent extraction, membrane separation, reverse osmosis, ultrafiltration, electrochemical deposition, ion exchange and adsorption [5]. Among these methods, adsorption methods considered as a simple, low-cost and effective method in removing heavy metals from water and wastewater [3,6–9]. A numbers of low-cost natural adsorbent materials have been evaluated for their capability of removing toxic metal ions, biogenic iron oxide is one of the natural low-cost adsorbents. Some research-

---

*Corresponding author.

ers have used various forms of Banded iron formation (BIF) for heavy metal removal from water and wastewater. *Leptothrix ochracea* type of biogenic iron oxide is used for Cu(II) ion removal from solutions [10]. The BIF material was studied for removal of 7 types of hazardous water-soluble organic dyes [11–14]. The arsenic and phosphorus is also removed through bioremediation by biogenic iron oxide and sulfides [15].

Huge layers of BIF a form of iron oxide, contains iron between 25 and 35 weight percentage [16]. BIF has distinctive units of natural sedimentary rocks that are almost of Precambrian age and available all around the world. BIF are produced by weathering activities or series of bacterial metabolic activities, passive reactions, and internal biomineralization processes. The natural biogenic iron oxides are produced by the metabolic activity of acediophilic and neutrophilic iron oxidizing bacteria which helps in oxidation of Fe(II) to Fe(III). Various forms of biogenic iron oxides are available on Earth's environment. Some type of bacterial-iron oxide associations have also been observed near the roots in the iron plaque of aquatic plants in wetlands [17–20]. Natural biogenic iron oxides in iron plaque form are produced by Gallionella capsiferriformans and found in the rhizosphere in type of *Typha Latifolia* form. It produces insoluble ferric hydroxide, which deposits iron plaque (Fe plaque) on wetland plant roots contains abundant microbial populations, including Fe(II) oxidizing bacteria (FeOB) [18,21,22]. The BIF and iron plaque forms of natural biogenic iron oxides have been considered for this study. In this work, the sorption of copper from aqueous solutions by BIF and iron plaque types of biogenic iron oxide are investigated. The sorption equilibrium data have been described by typical Langmuir, Freundlich and Redlich-Peterson sorption equations. The three kinetic models including simple first order rate equation, second-order rate equation, and pseudo first-order rate equation kinetic equation have been selected to follow the sorption process. The objective of the study is to obtain the adsorption capacity of Cu(II) ion by using BIF and iron plaque biogenic iron oxide as an adsorbent in batch system.

2. Material and methods

2.1. Biogenic iron oxides (BIF)

Dalli Rajhara in Durg (India) is home of iron ore captive mines for the integrated steel plant in India. Dalli mines deposit was discovered in 1900 and is located at 20.58°N 81.08°E. The natural biogenic iron oxide (Fe_2O_3) in BIF form (iron ore) were collected from iron ore mines located at Dalli-Rajhara. The iron ore was crushed and converted into powdered form, and then was passed through the geometric sieve 300, 150 and 75 µm size particles for collection of different size particles. BIF particles of different sizes were stored in plastic jars for batch experiment.

2.2. Iron plaque

The site of Sharda Canal is between 81° 7′ 15.75′ N and 20° 28′36.02′ E in Raebareli (India). The lake is perennial and very big in expanse, measuring about 300 m in length and 100 m in breadth at its widest. From this wetland, the plants species like *Typha-latifolia* were obtained, which had solid iron plaque particles in their roots. The roots of *Typha latifolia* were collected and washed with double distilled water. The eluent was collected in jar contain iron oxide particles. The particles were dried at 50°C for 2–3 h in hot air oven and converted into powdered form. It was then passed through the geometric sieve 300, 150 and 75 µm size particles for collection of different sizes particles. BIF particles of different size were stored in plastic jars for batch experiment.

2.3. Preparation of aqueous solution

The aqueous Cu(II) ion solution was prepared as per standard methods, APHA [23]. The 200 mg of polished electrolytic copper wire or foil was placed in 250 mL conical flask. 10 mL water and 5 mL concentration HNO_3 were then added. After slowdown the reaction, warm gently to complete dissolution of the copper and boil to expel oxides of nitrogen, using precautions to avoid loss of copper. It was cooled and about 50 mL water was added. This was then transferred quantitatively to a 1-L volumetric flask, and diluted to the mark with water; 1 mL = 200 µg Cu.

The concentration of Cu(II) ion in the solution was determined by Bathocuproine methods as described in the standard methods, APHA [23]. The absorbance was measured by UV/VIS spectrophotometer (Model: Lab India UV 3000$^+$, Lab India Analytical Instruments Pvt. Ltd) at 484 nm wavelength. The pH was determined by digital pH meter (Model: Cyber Scan pH 510/Ion 510, Eutech Instruments, Singapore).

2.4. Characterization of adsorbents

A small portion of absorbents were taken for morphological characterization. The environmental scanning electron microscope (ESEM) images were obtained by (Model: FEI Quanta 200F with Oxford-EDS system IE 250 X Max 80, the Netherlands) instrument. The energy dispersive x-ray spectroscopy (EDS) analysis was carried out to find out the normalized element composition (by weight percentage) and elemental spectra of adsorbent.

2.5. pH zero point charge (pH_{zpc})

The point of zero charge (pHzpc) of natural biogenic iron oxide BIF form was determined by using solid addition method with double distilled water and KNO_3 solutions. The 50 ml of double distilled water was transferred into a series of conical flasks and the initial pH (pHi) of these solutions were roughly adjusted between 2.0–10.0 by addition of either 0.1 N HCl or 0.1 N NaOH solutions. The initial pHs (pHi) of these solutions were measured accurately with the help of digital pH meter. Then 0.5 g of BIF media was added into each flask for 24 h with intermittent manual shaking. The final pHs (pHf) of these supernatants were measured accurately. The difference between the final (pHf) and initial pH (pHi) values (ΔpH = pHf – pHi) were plotted against pHi. The point of intersection of the resulting curve with abscissa at which ΔpH = 0 represents pHpzc. The same procedure was repeated using 0.01 N and 0.1 N KNO_3 solutions.

2.6. Adsorption experiment

The batch adsorption experiments were conducted on both BIF crystal and iron plaque sorbents separately in 250 mL beaker using horizontal shaker machine. The 100 mL of 20 mg/L Cu(II) ion concentration of standard solutions were placed in 250 mL beakers. The 40 g/l sorbent dose of 300, 150 and 75 µm media size was added to each reaction mixture. The solution was agitated in an orbital shaker incubator at 170 rpm at 20°C ± 2°C temperature for 3 h. The percentage of removed Cu(II) ion was calculated using Eq. (1):

$$R[\%] = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

The amount of adsorbed Cu(II) per mass unit of adsorbent at equilibrium 'q_e' (mg/g) was calculated using Eq. (2) [6].

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{2}$$

The adsorption capacity 'q_t' at time 't' was determined using Eq. (3) [24].

$$q_t = \frac{V(C_0 - C_t)}{M} \tag{3}$$

where C_0 and C_t are Cu(II) ion concentrations in mg/L at initially time 't' at zero or at given time t. C_e is the concentration of Cu(II) ion in solution in mg/L at equilibrium, V is the volume of initial metal ions solution in liters and M is mass of adsorbent in gram.

The Langmuir model [25] describes monolayer sorption on to a surface of adsorbent. It is used to estimate the maximum metal sorption at saturation level reached in the experiment. The non-linear form of Langmuir isotherm model is presented by Eq. (4).

$$q_e = \frac{Q_o b C_e}{1 + bC_e} \tag{4}$$

Eq. (4) can be expressed in its linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{5}$$

Any of these two Eqs. (4) and (5) may be used to evaluate Langmuir constants Q_0 and b from experimental data using graphs or least square analysis.

The Freundlich isotherm [26] based on multilayer adsorption states that the surface of sorbent was heterogeneous and adsorption on non-uniform distribution of heat of sorption. The Freundlich isotherm model can be described by Eq. (6) [27].

$$q_e = K_f C_e^{1/n} \tag{6}$$

Eq. (6) can be expressed in its linear form by Eq. (7).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{7}$$

where K_f and n are Freundlich constants, K_f is the adsorption capacity of the adsorbent (mg g^{-1} (L mg^{-1})$^{1/n}$) and n is a constant indicative of intensity of adsorption.

The Redlich-Peterson isotherm represents a mixture of the Langmuir and Freundlich isotherms. The numerator is from the Langmuir isotherm and has the benefit of approaching the Henry region at infinite dilution. The denominator has the mixture Langmuir-Freundlich form isotherm and may represent the adsorption equilibria over a wide concentration range. The Redlich-Peterson isotherm is represented by Eq. (8) [28].

$$q_e = \frac{A_2 C_e}{1 + B_2 C_e^{\,n}} \tag{8}$$

The linear form of Redlich-Peterson isotherm is written as

$$\frac{C_e}{q_e} = \frac{B_2 C_e^{\,n}}{A_2} + \frac{1}{A_2} \tag{9}$$

where q_e (mg/g) represents the adsorbed metal ion concentration at equilibrium, C_e represents the residual metal ion concentration at equilibrium and n is the Freundlich adsorption intensity constant, both A_2 and B_2 are fitting parameters. A_2 and B_2 can be calculated by fitting the data of batch adsorption experiment into this model.

Contact time from experimental results may be used for the study of rate-limiting step in the adsorption process in terms of the kinetic energy. An attempt has been made in mathematical approach for kinetic modeling of uptake of Cu(II) ion onto BIF form of biogenic iron oxide for determination of kinetic parameters. Adsorption kinetics may also be described by simple first order rate equation [29,30] represented by Eq. (10).

$$C_t = C_{\circ} e^{k_1 t} \tag{10}$$

The linear form of simple first order rate equation can be written as Eq. (11).

$$\log C_t = \frac{k_1}{2.303} t + \log C_o \tag{11}$$

where k_1 (1/min) is the first order rate constant.

The linear form of second-order rate equation is written as Eq. (12) [31].

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_3 t \tag{12}$$

where k_3 (g mg^{-1} min^{-1}) represents the second order rate constant.

Rate of sorption is a function of number of parameters such as physical and chemical characteristics of sorbent, initial concentration and nature of solute etc. In order to examine the controlling mechanism of the adsorption process, pseudo first-order rate equation was used and represented by Eq. (13) [31,32].

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{13}$$

Eq. (13) can be expressed linearly as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{14}$$

The Roginsky-Zeldovich or Elovich kinetic equation can be expressed generally as given by Eq. (15) [33,34].

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_t) \tag{15}$$

3. Results and discussions

3.1. Characterization of adsorbents

The small portion of both BIF crystal and iron plaque absorbents were intended for morphological characterization. The ESEM images were obtained at an accelerating voltage of 10 kV for 15000x and 30000x for BIF crystals and 3.00 kV for 100000x and 25000x for iron plaque particle. The surface morphology of BIF crystal by ESEM (Fig. 1) revealed that surface is rough due to deposition of Fe_2O_3 hematite. The surface morphology of iron plaque particle of *Typha-latifolia* (Fig. 2) does not reveal clearly any deposition of $Fe(OH)_3$ (ferric hydroxide) on its surface.

The EDS spectra of BIF crystal represents the elemental composition in percentage of iron, silica, aluminium, oxygen and carbon. Similarly, iron plaque represents the elemental composition in percentage of iron, calcium, silica, aluminium, magnesium, oxygen and carbon particles as shown in (Fig. 3) and (Table 1), respectively. From the ESEM and EDS analysis, the BIF crystal shows 60.4 % iron (Fe) as compared with iron plaque particle having iron (Fe) 12.38%.

3.2. pHzpc of BIF

Anion can be adsorbed on adsorbents through nonspecific and/or specific adsorption. Nonspecific adsorption involves the coluombic forces, and is mainly limited to pH dependent sites below pHzpc (the pH value at which surface charge is zero) of the adsorbent. The adsorbent gets positively charged when the solution pH is below pHzpc and attracts the anions of the synthetic wastewater. The adsorbent gets negatively charged when solution pH is greater

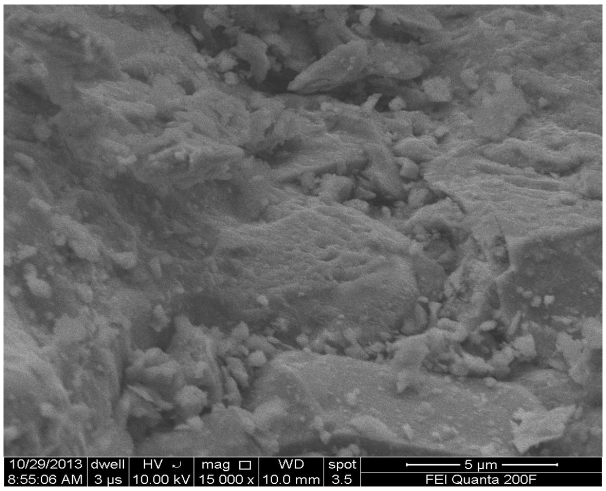


Fig. 1. ESEM micrograph of BIF form adsorbent at 15000×.

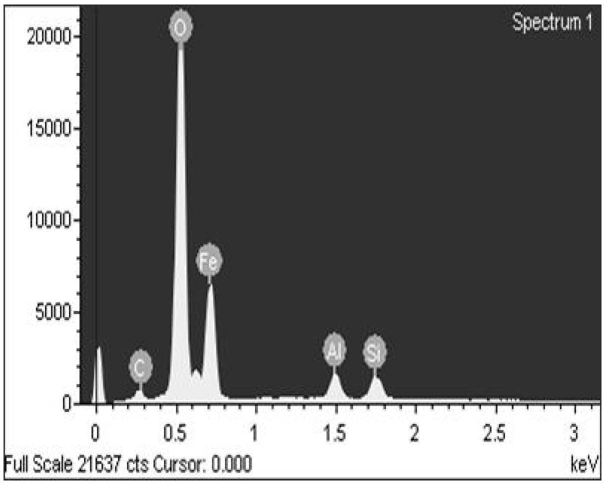


Fig. 3. EDS spectra of BIF crystal and iron plaque of *Typha-latifolia* adsorbent.

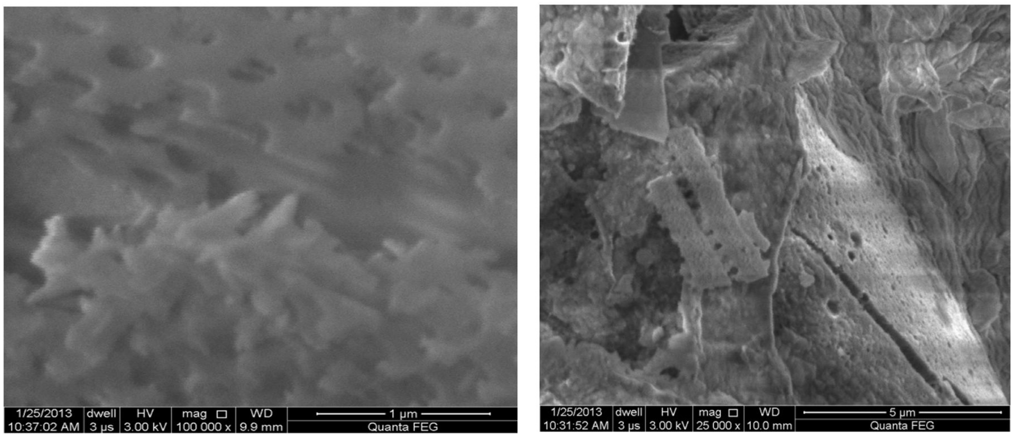


Fig. 2. ESEM micrograph of iron plaque particle of *Typha-latifolia* at (a) 100000× and (b) 25000×.

than the pHzpc and hence it attracts the cations. The pHzpc was determined and result is presented in Fig. 4. In the present study, the pHzpc 5.2 was found for BIF adsorbent.

The pH_{zpc} value indicates that BIF adsorbent media is positively charged at neutral pH, researcher reported the hematite having pH_{zpc} between 5–9 [35]. The measured pH_{zpc} value of BIF adsorbent (Fe_2O_3) media in the present study falls near this pH range. It probably due to incorporation of some cations into Fe oxides, which can increase pH_{zpc} of media. From the result this also suggests from the result that the iron oxide is dominated, at least in the acid base interaction between surface solutions. There is a similarity between these results and previous results obtained by other researcher [36].

Table 1
Normalized element composition (wt.%) of natural biogenic iron oxide

Banded iron formation			Iron plaque particle of *Typha-Latifolia*		
Element	Weight	Atomic	Element	Weight	Atomic
C K	2.04	4.89	C K	4.17	7.15
O K	33.07	59.41	O K	48.56	62.52
Al K	2.11	2.25	Mg K	6.67	5.65
Si K	2.23	2.29	Al K	7.87	6.01
Fe L	60.54	31.16	Si K	16.62	12.19
Totals	100.00		Ca K	3.73	1.92
			Fe L	12.38	4.57
			Totals	100.00	

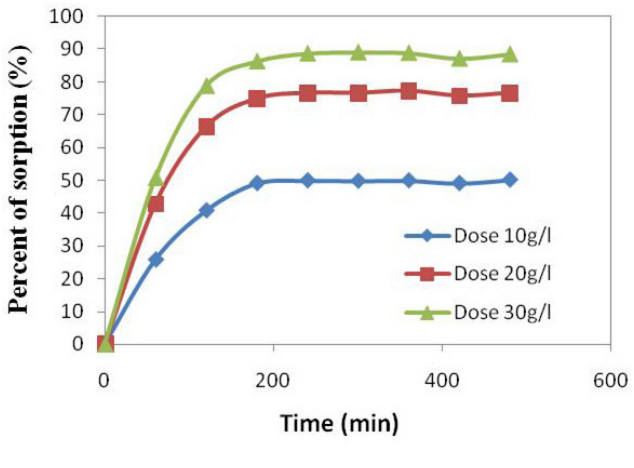


Fig. 4. Effect of contact time on the sorption of Cu(II) ion.

3.3. Adsorption experiments

The batch adsorption experiments were conducted on both BIF crystal and iron plaque sorbent separately. The natural biogenic iron oxide, BIF crystal have shown better Cu(II) ion removal, about 70.5%, than iron plaque particle (9.62%) as show in Table 2 under same conditions. The adsorption capacity for Cu(II) ion on both sorbent increased with decrease of media size and the maximum removal capacity was found to be 0.3525 mg/g for BIF and 0.0481 mg/g for iron plaque particle. Compared with similar work, the adsorption capacity for removal of Cu(II) ion about 34.84 mg/g for nano-hematite [37] and 9.94 mg/g for maghnite [38]. The BIF crystal shows better sorption potential as compared to iron plaque particle, and therefore all types of batch experiments were conducted using BIF crystal of 75 µm size.

Sorption study was conducted by batch experiments for removal of Cu(II) ion by BIF. The 100 mL of 20.0 mg/L concentrated sorbate solution at pH 5 was taken. The experiments were performed for effects of sorbent dose on Cu(II) ion removal with different doses of 10, 20 and 30 g/l of 75 µm size of BIF sorbent added to the each set of reaction mixtures. It was agitated in orbital shaker incubator at 170 rpm at 20°C ± 2°C temperature for 480 min. Samples were collected at 60, 120, 180, 240, 300, 360, 420 and 480 min interval of time and then analyzed for residual Cu(II) ion concentration.

The Cu(II) ion removal increases as the adsorbent dose of BIF crystal increases as shown in (Fig. 6a). In the batch system the rate of adsorption increases initially and then almost stabilizes after 240 min. Equilibrium of Cu(II) ion was attained at 240 min. The removal was almost stabilized after 240 min implying that the equilibrium has been reached. The maximum percentage removal was 50, 76.75 and 88.65%. The adsorption capacity at equilibrium was observed 1, 0.767 and 0.591 mg/g for 10 g/l, 20 g/l and 30 g/l adsorbent dose respectively. The optimum adsorbent dose of BIF crystal was found 30 g/l and the maximum removal efficiency was 88.65%. As compared to the similar works, about 89% Cu(II) ion removal was found by hematite [39] 83.50% by $NiFe_2O_4$ [40] and 95% by iron oxide (α-Fe_2O_3) nanoparticles [41].

The adsorption isothermal studies were carried out on BIF adsorbent under same conditions. The adsorption is in line with the Langmuir and Freundlich adsorption isotherms. The Langmuir plot of $1/q_e$ versus $1/C_e$ with a high regression coefficient (R^2) value of 0.987 is shown in

Table 2
Cu(II) ion removal efficiency by both forms of natural biogenic iron oxid

Media size (µm)	Dose (g)	C_0 (mg/L)	Batch time (h)	BIF		Iron plaque of *Typha-Latifolia*	
				Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)
300	4	20	3	40	0.2025	6.4	0.032
150	4	20	3	58.33	0.29175	8.4	0.042
75	4	20	3	70.5	0.3525	9.62	0.0481

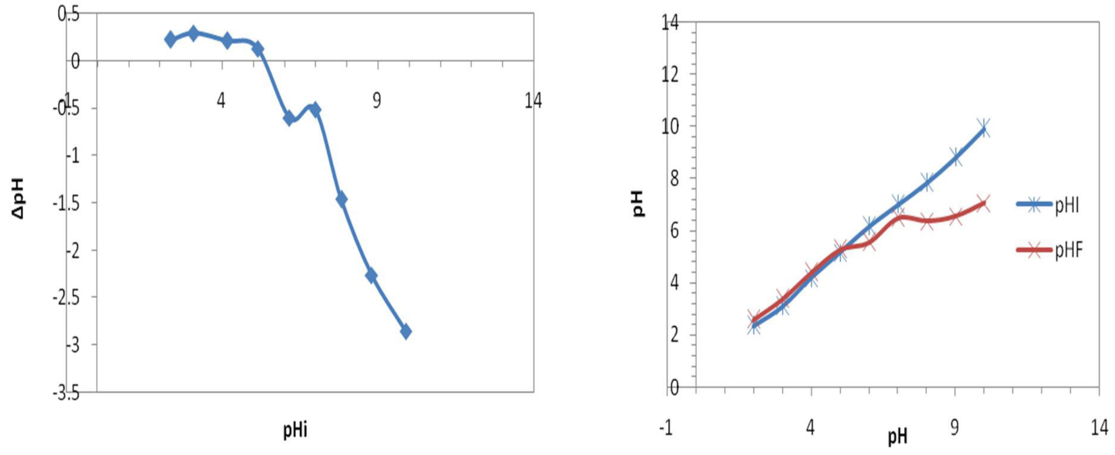
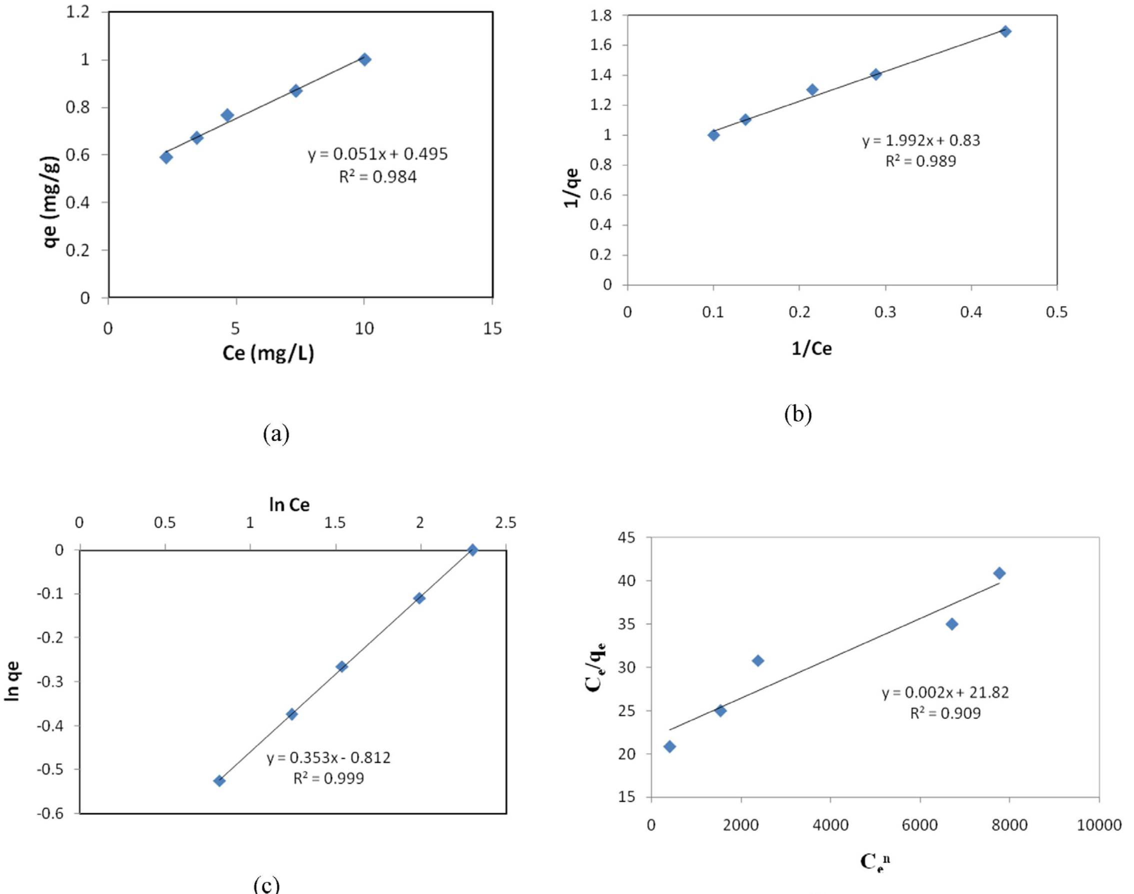


Fig. 5. pHzpc of the media.



(a)

(b)

(c)

(d)

Fig. 6. Adsorption isotherms of Cu(II) on BIF adsorbent [Adsorbent Size 75 µm; Initial Cu(II) conc. 20 mg/l, pH 5 at 20°C ± 2°C; 170 rpm] (a) Curve of adsorption isotherm (q_e~C_e) (b) Langmuir isotherms (c) Freundlich isotherm (d) Redlich-Peterson Isotherm.

Fig. 6b. The plot is linear with high adsorption capacity (Q_0) of 1.204 mg/g and binding capacity (b) of 2.401 L/mg. The Freundlich isotherm plot of ln q_e vs. ln C_e is shown in Fig. 6c with a very high regression coefficient (R^2) value of 0.999. The Freundlich constant $1/n$ was (0.353) smaller than 1 indicating a favourable adsorption process. The Freundlich exponent n value is 2.832 lying in the range of 1 to 10 which is favourable for chemical adsorption ($n < 1$) [42]. The Redlich-Peterson mode for Cu(II) ion adsorption onto BIF adsorbent based on different dose is shown in Fig. 6d.

Redlich-Peterson isotherm predicted very low correlation coefficient (R^2) value of 0.909 suggesting that experimental equilibrium relationship does not fit by Redlich-Peterson isotherm over concentration range. The Langmuir, Freundlich and Redlich-Peterson isotherms constants are shown in (Table 3).

The modeling of adsorption kinetics were evaluated using batch experiment kinetic data of different adsorbent doses. The simple first order kinetic plot for Cu(II) ion adsorption onto BIF adsorbent is shown in Fig. 7. The data is fitted to simple first order kinetic model and kinetic parameters shown in Table 4. The correlation coefficient (R^2) values are 0.548, 0.918, and 0.918 for 10 g/l, 20 g/l and 30 g/l adsorbent doses, respectively. There is a similarity between these results and previous results obtained by other researchers [43,44]

The second order rate equation kinetic plot for Cu(II) ion adsorption onto BIF adsorbent is presented in Fig. 8. The correlation coefficient (R^2) values are 0.53, 0.462, and 0.48 for 10 g/l, 20 g/l and 30 g/l adsorbent doses in second order kinetic model and suggest that adsorption kinetics is not applicable on second order kinetic model. [45] reported that the simple kinetic models such as first or second order rate equations are not applicable to the adsorption system with solid surfaces due to their rare homogenity.

Similarly, the pseudo first order kinetic plot of log (q_e–q_t) vs. t (min) is shown in Fig. 9. The high correlation coefficients (R^2) were 0.944, 0.986 and 0.999 for 10 g/l, 20

Table 3
Adsorption capacities and correlation coefficient for Cu (II) sorption on adsorbents

Langmuir isotherms	Q_o mg/g	b L/mg	*Ks*	R^2
	1.204	2.401	0.0203	0.987
Freundlich isotherms	K_f (mg g^{-1} (L mg^{-1})$^{1/n}$)	$1/n$	n	R^2
	0.4439	0.353	2.832	0.999
Redlich-peterson	A_2	B_2	n	R^2
	0.0456	0.0001	2.8571	0.909

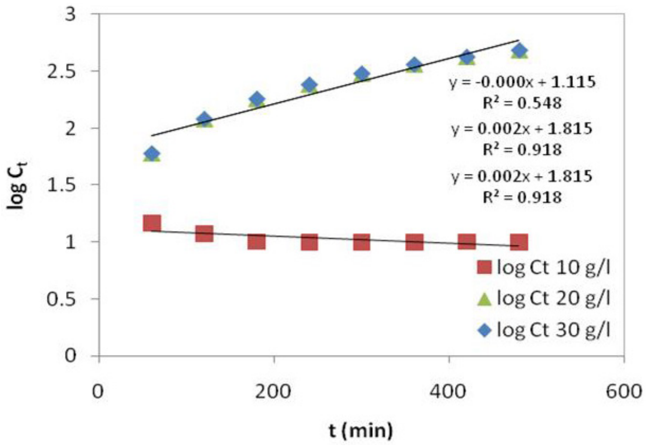


Fig. 7. Simple first order kinetic plot for Cu(II) ion adsorption (Conditions: adsorbent size 75 μm; initial Cu(II) ion conc. 20 mg/l, pH 5 at 20°C ± 2°C; 170 rpm).

Table 4
Different kinetic parameters of Cu(II) ion adsorption using BIF adsorbent

Dose	Simple first order rate equation			
	q_e exp. mg/g	k_1 (1/min)		R^2
10 g/l	1	0		0.548
20 g/l	0.767	0.0046		0.918
30 g/l	0.591	0.0046		0.918
	Second order rate equation			
	k_3 g mg^{-1} min^{-1}	q_e mg/g		R^2
10 g/l	0	3.1546		0.53
20 g/l	0	1.3495		0.462
30 g/l	0	0.7968		0.48
	Pseudo first order model/Langergren first-order rate equation			
	k_1 min^{-1}	q_e^{cal} mg/g	q_e^{exp} mg/g	R^2
10 g/l	0.0276	3.2509	1	0.944
20 g/l	0.0230	1.6749	0.767	0.986
30 g/l	0.0230	1.0162	0.591	0.999

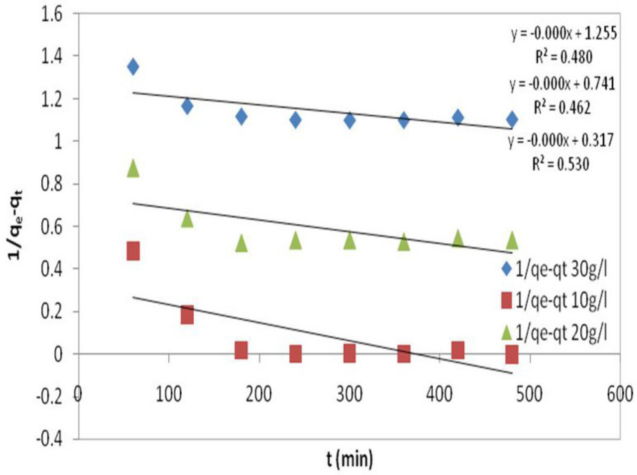


Fig. 8. Second order rate equation kinetic plot for Cu(II) ion adsorption (Conditions: adsorbent size 75 μm; initial Cu(II) ion conc. 20 mg/l, pH 5 at 20°C ± 2°C; 170 rpm).

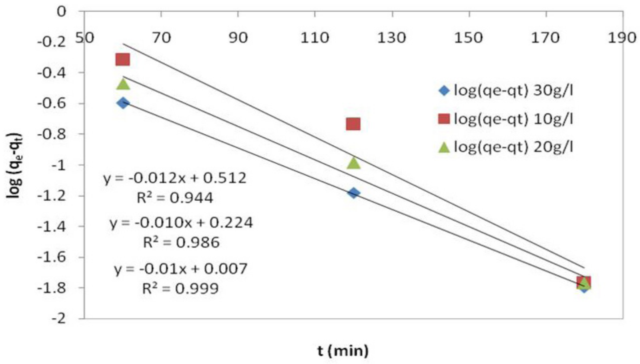


Fig. 9. Pseudo first order kinetic plot for Cu(II) ion adsorption (Conditions: adsorbent size 75 μm; initial Cu(II) ion conc. 20 mg/l, pH 5 at 20°C ± 2°C; 170 rpm).

g/l and 30 g/l adsorbent doses, respectively. The q_e and k_1 were calculated from the intercept and slope respectively from Fig. 9. The plot was negatively sloped and the experimental equilibrium adsorption capacity (q_e^{exp}) was not in proper agreement with the calculated equilibrium adsorption capacity (q_e^{cal}). This means that adsorption of Cu(II) ion could not have complete fit with this kinetic model. According to the linear coefficients of determination, (R^2) values represented in Table 4 are more than 0.94 Pseudo first order kinetic model. The total Cu(II) ion adsorption is better fitted to Pseudo first order kinetic model.

4. Conclusions

The results obtained in this study demonstrate that natural biogenic iron oxide of BIF form can be used as an excellent adsorbent to remove copper (II) ions from wastewaters with a good efficiency with low cost. The BIF crystal has maximum removal potential as compared to iron plaque particle of *Typha-latifolia*. Several parameters were studied on BIF crystal and the maximum sorption efficiency was 88.65% at 30 g/l adsorbent dose. The Freundlich isotherm best fitted with (R^2) value of 0.999 are compared with Langmuir isotherm and Redlich-Peterson isotherm. The maximum adsorption of 2.303 mg/g for Cu(II) removal were obtained according to the Freundlich adsorption isotherm. The Pseudo first order had been fitted to describe the batch kinetics of the Cu(II) uptake by BIF. This study suggests that natural biogenic iron oxide of BIF form may be used as a viable adsorbent for the removal of copper (II) metal ions from water and wastewaters.

References

[1] H.G. Seiler, A. Sigel, H. Sigel, Handbook on toxicity of inorganic compounds, Marcel-Dekker, New York, 1998.

[2] M. Mukhopadhyay, S.B. Noronha, G.K. Suraishkumar, Kinetic modeling for the bioadsorption of copper by pretreated Aspergillus niger biomass, Bioresour. Technol., 98 (2007) 1781–1787.

[3] J.W. Patterson, Industrial wastewater treatment technology, 2nd ed., Stoneham, MA: Butterworths Publishers, 1985.

[4] R. Gundogan, B. Acemioglu, M.H. Alma, Copper (II) adsorption from aqueous solution by herbaceous peat, J. Colloid Interf. Sci., 269 (2004) 303–309.

[5] P. Cloud, Paleoecological significance of the banded iron formation, Econ. Geol., 68 (1973) 1135–1143.

[6] Jr. M. Horsfall, I. Ayebaemi, A.A. Abi, Studies on the influence of mercaptoacetic acid (MAA) modification of cassava (Manihot Sculenta Cranz) waste biomass on the adsorption of Cu^{2+} and Cd^{2+} from aqueous solution, Bullet. of the Korean Chem. Soci., 25 (2004) 969–976.

[7] D.G. Lundgren, W. Dean, Biogeochemistry of iron, In: Trudinger, P.A., Swaine, D.J. (eds.), biogeochemical cycling of mineral-forming elements, Sci. Publ. Comp., (1979) 211–251.

[8] D.E. Weiss, Bacterial iron oxidation in circumneutral freshwater habitats: findings from the field and the laboratory, Geomicrobi. J., 21 (2004) 405–414.

[9] R. Katal, H. Zare, S.O. Rastegar, P. Mavaddat, G.N. Darzi, Removal of dye and chemical oxygen demand reduction from textile industrial wastewater using hybrid bioreactors, Environ. Eng. Manag. J., 13 (2014) 43–50.

[10] J.A. Rentz, J.L. Ullman, Copper and zinc removal using biogenic iron oxides, World Environ. Water Res. Congress: Crossing Boundaries, 2012.

[11] A.B. Seabra, P. Haddad, N. Duran, Biogenic synthesis of nanostructured iron compounds: applications and perspectives, IET Nanobiotechnol., 7 (2013) 90–99.

[12] H. Katerina, S. Ivo, F. Jan, N. Maryla, T. Jiri, S. Mirka, H. Hideki, T. Jun, Z. Radek, Magnetically responsive natural biogenic iron oxides for organic xenobiotics removal, Nanocon, 16–18 Oct., Brno, Czech Republic, EU, 2013.

[13] E.O. Omoregie, R.M. Couture, P.V. Cappellen, C.L. Corkhill, J.M. Charnock, D.A. Polya, D. Vaughan, K. Vanbroekhoven, J.R. Lloyd, Arsenic bioremediation by biogenic iron oxides and sulphides, Appl. Environ. Microbiol., 79 (2013) 4325–4335.

[14] A.J. Williams, D.Y. Sumner, C.N. Alpers, K.M. Campbell, D.K. Nordstrom, Biogenic iron mineralization at iron mountain, ca, with implications for detection with the mars curiosity rover, 45th Lunar and Planetary Science Conference, 2014.

[15] G.M. Ayoub, H, Kalinian, Removal of low-concentration phosphorus using a fluidized raw dolomite bed, Water Env. Res., 78 (2006) 353–361.

[16] H.L. James, P.K. Sims, Precambrian iron-formations of the world, Econ. Geol., 68 (1973) 913–914.

[17] L. St-Cyr, D. Fortin, P.G.C. Campbell, Microscopic observations of the iron plaque of a submerged aquatic plant (Vallisneria americana Michx), Aquat. Bot., 46 (1993) 155–167.

[18] D. Emerson, J.V. Weiss, J.P. Megonigal, Iron-oxidizing bacteria are associated with ferric hydraoxide precipitates (Fe-Plaque) on the roots of wetland plants, Appl. Environ. Microbiol., (1999) 2758–2761.

[19] S.A. Figueiredo, O. Matos Freitas, Adsorption kinetics of removal of yellow lanasol dyestuff using gallinaceous feathers, Environ. Eng. Manage. J., 12 (2013) 2061–2070.

[20] C.J. Igwe, U. Arukwe, N.S. Anioke, Isotherm and kinetic studies of residual oil adsorption from palm oil mill effluent (pome) using boiler fly ash, Environ. Eng. # Manage. J., 12 (2013) 417–427.

[21] J.V. Weiss, Characterization of neutrophilic Fe(II) oxidizing bacteria isolated from the rhizosphere of wetland plants and description of Ferritrophicum radicicola gen. nov. sp. nov., and Sideroxydans paludicola sp. Nov, Geomicrobi. J., 24 (2007) 559–570.

[22] S.C. Neubauer, G.E. Toledo-Duran, D. Emerson, Returning to their roots: iron-oxidizing bacteria enhance short-term plaque formation in the wetland-plant rhizosphere, Geomicrobiol. J., 24 (2007) 65–73.

[23] APHA, Standard methods for the examination of water and wastewater". 22rd edition. American Public Health Association, American Water Works Association, Water Environment Federation, 2012.

[24] A. Demirbas, Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignication, J. Hazard. Mater., 109 (2004) 221–226.

[25] I. Langmuir, The Constitution and fundamental properties of solids and liquids, Part I, Solids, J. Amer. Chem. Soc., 38 (1916) 2221–2295.

[26] H.M.F. Fruindlich, Under die adsorption in Losungen, J. Phys. Chem., 57 (1906) 385–470.

[27] L. Liu, J. Liu, H. Li, H. Zhang, J. Liu, H. Zhang, Lead biosorption on sesame leaf, BioResour., 7 (2012) 3555–3572.

[28] J.A. Rentz, I.P. Turner, J.L. Ullma, Removal of phosphorus from solution using *Leptothrix sp*, Water Res., 43 (2009) 2029–2035.

[29] C.A. Eligwe, N.B. Okolue, Adsorption of iron (II) by a Nigerian brown coal, Fuel, 73 (1994) 569–572.

[30] M.A. Hossain, M. Kumita, Y. Michigami, S. Mori, Kinetics of Cr(VI) adsorption on used black tea leaves, J. Chem. Eng. Japan, 38 (2005) 402–406.

[31] S. Ghorai, A.K. Sarkar, A.B. Pand, S. Pal, Effective removal of congo red dye from aqueous solution using modified xanthan gum/silica hybrid nanocomposite as adsorbent, Bioresour. Technol., 144 (2013) 485–491.

[32] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (1898) 1–39.

[33] M.J.D. Low, Kinetics of chemisorption of gases on solids, Chem. Rev., 60 (1960) 267–312.

[34] Y.S. Ho, G. McKay, Application of kinetic models to the sorption of copper (II) on to peat, Adsorp. Sci.Technol., 20 (2002).

[35] J.I. Drever, The geochemistry of natural waters, Prentice-Hall, New Jersey, 1997.

[36] R.A.K. Rao, S. Ikram, Sorption studies of Cu(II) on gooseberry fruit (*emblica officinalis*) and its removal from electroplating wastewater, Desalination, 277 (2011) 390–398.

[37] Y.H. Chen, F.A. Li, Kinetic study on removal of copper(II) using goethite and hematite nano-photocatalysts, J. Colloid Interface Sci., 347 (2010) 277–281.

[38] M.A. Zenasni, S. Benfarhi, A. Merlin, S. Molina, B. George, B. Meroufel, Adsorption of Cu(II) on maghnite from aqueous solution: Effects of pH, initial concentration, interaction time and temperature, Natural Sci., 4 (2012) 856–868.

[39] H.J. Shipley, K.E. Engates, V.A. Grover, Removal of Pb(II), Cd(II), Cu(II), and Zn(II) by hematite nanoparticles: effect of sorbent concentration, pH, temperature, and exhaustion, Environ. Sci. Pollut. Res., 20 (2013) 1727–1736.

[40] N. Sezgin, M. Sahin, A. Yalcin, Y. Koseoglu, Synthesis characterization and the heavy metal removal efficiency of MFe_2O_4 (M=Ni, Cu) Nanoparticles, Ekoloji, 22 (2013) 89–96.

[41] K.A. Al-Saad, M.A. Amr, D.T. Hadi, R.S. Arar, M.M. AL-Sulaiti, T.A. Abdulmalik, N.M. Alsahamary, J.C. Kwak, Iron oxide nanoparticles: applicability for heavy metal removal from contaminated water, Arab J. Nucl. Sci. Appl., 45 (2012) 335–346.

[42] A.M. Farhan, A.H. Al-Dujaili, A.M. Awwad, Equilibrium and kinetic studies of cadmium(II) and lead(II) ions biosorption onto Ficus carcia leaves, Int. J. Ind. Chem. 4 (2013) 24.

[43] R. Khandanlou, M.B. Ahmad, H.R.F. Masoumi, K. Shameli, M. Basri, K. Kalantari, Rapid adsorption of copper(II) and lead(II) by rice straw/Fe_3O_4 nanocomposite: optimization, equilibrium isotherms, and adsorption kinetics study, PLoS ONE, 10(3) (2015) 45–53.

[44] J. Sun, G.L. Yu, L.L. Liu, Z.F. Li, Q.B. Kan, Q.S. Huob, Core-shell structured Fe_3O_4@SiO_2 supported cobalt(II) or copper(II) acetylacetonate complexes: magnetically recoverable nanocatalysts for aerobic epoxidation of styrene, Catal. Sci. Technol., 4 (2014) 1246–1252.

[45] D.L. Sparks, Kinetics of Soil Chemical Processes, 1st ed., Academic Press, New York, USA, 1989, pp. 18–29.