Adsorptive removal of copper(II) from aqueous solutions using low cost Moroccan adsorbent.
Part II: Kinetic and equilibrium studies

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Abstract

Adsorption can be an efficient low-cost process to remove toxic heavy metals from wastewater. This study investigated the efficiency of treated Martil sand (TMS) in the removal of copper(II). Adsorption equilibrium data were calculated for Langmuir and Freundlich isotherms. It was found that the sorption of Cu(II) was better suited to the Freundlich adsorption model than to the Langmuir adsorption model. The results showed that non-linear method could be a better way to obtain the isotherm parameters. Kinetic data were analyzed using different models, namely, the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, the intraparticle diffusion model and the Elovich equation model. Among all these kinetic models, it was observed that the pseudo-second-order model was the best choice describing the adsorption behavior of Cu(II) onto treated Martil sand. This suggested that the adsorption mechanism might be a chemisorption process.

Keywords: Martil sand, Copper(II), Adsorption, Isotherms, Kinetic, Desorption and regeneration.

1. Introduction

Adsorption has been an effective separation process for a wide variety of applications. In the endeavor to explore novel adsorbents in accessing an ideal adsorption system, it is essential to establish the most appropriate adsorption equilibrium correlation [1]. Equilibrium relationships, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and they are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems [2,3]. Thus, an accurate mathematical description of the equilibrium isotherms is essential to the effective design of sorption systems.

The adsorption isotherms are equilibrium equations and applied to condition resulting after the adsorbate containing phase have been in contact with the adsorbent for sufficient time to reach equilibrium at a constant temperature. The different parameters of these equilibrium models often provide some insight into the sorption mechanism, the surface properties and affinity of sorbent. Among the isotherm equations that can explain solid–liquid adsorption systems, Langmuir and Freundlich are the most commonly used isotherms by several

researchers for different sorbent/sorbate systems [4−8]. Linear regression was frequently used to determine the most fitted isotherms. The linear least-squares method with linearly transformed isotherm equations was widely applied to confirm the experimental data and isotherms using coefficient of determination [9]. However, previously researchers showed that, depending on the way isotherm equation is linearized, the error distribution changes either the worse or the better [10]. So, it will be an inappropriate technique to use only the linearization method for estimating the equilibrium isotherm parameters.

Taking into account these considerations, the main objective of this study is to assess the effectiveness of treated Martil sand (TMS) in the removal of copper by determining the maximum adsorption capacity. Langmuir and Freundlich adsorption isotherm models were used to fit the equilibrium isotherm. The adsorption isotherm parameters of these models were determined using linear and non-linear method. The adsorption kinetic was examined using four kinetic models, the pseudo-first-order equation, the pseudo-second-order equation, the Elovich equation, and the intraparticle diffusion equation.

2. Experimental
2.1. Materials
The sea sand (NMS) used was collected from Martil Beach located at the north west of Morocco on the Mediterranean Sea. After collection, stones and other heavy particles were removed from the sample. Subsequently, the NMS was soaked in concentrated nitric acid (14.6 M) for 1 h and then washed thoroughly to remove all acid. Finally, the washed sample was dried in oven at 100 °C for 24 h, grounded and sieved. The obtained sample, named hereafter treated Martil sand (TMS), was sieved and the size of particles used in sorption tests was in the range: 125−180 μm.

All reagents used were of analytical grade and employed without any further purification. Aqueous solutions of copper Cu(II) at various concentrations were prepared by dissolving the appropriate amount of copper salt ($CuSO_4.5H_2O$) in deionized water.

2.2. Methods
2.2.1. Adsorption and kinetic experiments
Adsorption equilibrium experiments were conducted at room temperature by a batch method. Sorbent TMS samples (5 g) were equilibrated with 25 mL of 250 mg L^{-1} Cu(II) solution. The mixture was agitated for 10 h to assure the adsorption equilibrium. The solid was separated by centrifugation and the filtrate was analyzed by a flame atomic absorption spectrophotometer (Jobin Yvon 2) to determine the residual copper concentration. The pH of the solutions was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH. Isotherm and kinetic studies were carried out at constant pH 4 and 5 g of adsorbent at various Cu(II) concentrations (200−500 mg L^{-1}) at room temperature. Each experiment was duplicated under identical conditions.

2.2.2. Desorption and regeneration studies
Regeneration of the adsorbent was also important aspects of wastewater treatment. Desorption study was carried out using 5 g of the adsorbent, which was brought into contact with 25 mL of Cu(II) solution (250 mg L^{-1}). After adsorption experiment, Cu(II) loaded TMS was collected by filtration and washed several times with distilled water to remove any Cu(II) residual on the surface. Subsequently it was transferred to 50 mL desorbent solutions: deionised water, HCl, HNO_3, CH_3COOH, NaCl, Na_2SO_4 and EDTA being the concentrations of all acids and salts 0.1 M. The mixtures were shaken during 24 h, then the filtrates were analyzed to determine the concentration of Cu(II) after desorption. In order to reuse the adsorbent, HCl 0.1 M was used. The eluted adsorbent was washed repeatedly with distilled water to remove any residual desorbing traces. The adsorbent was subsequently used for re-sorption studies. The adsorption/desorption experiments were repeated three times.

2.3. Theoretical background
2.3.1. Adsorption isotherms
The percentage removal of copper ions and the adsorption capacity of the adsorbent at equilibrium, q_e (mg g^{-1}), were calculated using the following equations:

$$\% \, Adsorption = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

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

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentration of copper ion solution respectively, V is the volume of the solution (L) and m is the amount of adsorbent used (g).

Equilibrium sorption was modeled using the Langmuir and the Freundlich isotherms because they are the most commonly used due to their simplicity and ease of interpretation. The Langmuir model considers that the sorbent surface contains only one type of binding site and sorption of one ion per binding site is taking place. This can be described as

$$q_e = \frac{K_L q_{max} C_e}{1 + C_e K_L} \tag{3}$$

where q_e is the metal uptake, q_{max} is the maximum adsorption capacity and K_L is a constant related to adsorption energy. The Langmuir parameters can be determined from the slope and intercept when plotting C_e/q_e versus C_e, based on a linearized form of Eq. (3) and written as

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \tag{4}$$

The empirical Freundlich model considers no surface saturation and can be expressed as

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f and n are model constants that can be determined from the slope and intercept when log q_e is plotted versus log C_e, according to the linearized form of Eq. (5):

$$\log q_e = \log K_f + 1/n \, \log C_e \tag{6}$$

2.3.2. Kinetic models

In order to analyze the adsorption kinetics of TMS, four kinetic models, the pseudo-first-order equation, the pseudo-second-order equation, the Elovich equation, and the intraparticle diffusion equation were considered [11].

The pseudo-first-order reaction equation of Lagergren was widely used for the adsorption of liquid/solid system on the basis of solid capacity. Its linear form is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{7}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption amount at equilibrium and time t (min), respectively; and k_1 (min^{-1}) is the rate constant in the pseudo-first-order adsorption process. The values of q_e and k_1 can be determined from the intercept and the linear plot of $\log(q_e - q_t)$ versus t.

The pseudo-second-order model is based on the assumption that the adsorption follows a second-order chemisorption. Its linear form was written as

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \tag{8}$$

and $h = k_2 q_e^2$ (9)

where k_2 and h are the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}) and the initial sorption rate of pseudo-second-order adsorption (mg g^{-1} min^{-1}), respectively.

The possibility of intraparticle diffusion resistance affecting adsorption was explored by using the intraparticle diffusion model as

$$q_t = k_i t^{1/2} + C \tag{10}$$

where C is the intercept and k_i (mg g^{-1} min$^{1/2}$) is the intraparticle diffusion rate constant, which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$.

The Elovich equation model is expressed as follows:

$$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta} \tag{11}$$

where α (mg g^{-1} min^{-1}) is the initial adsorption rate and β (g mg^{-1}) is Elovich's parameter associated with the degree of coverage of adsorbent surface and energy of chemisorption [12].

2.3.3. Modeling error analysis
In order to evaluate the error of the model predictions, the coefficient of determination (R^2) was calculated for isotherm models and written as [13]:

$$R^2 = \frac{(q_{e,mes} - \overline{q_{e,cal}})^2}{\sum[(q_{e,mes} - \overline{q_{e,cal}})^2 + (q_{e,mes} - q_{e,cal})^2]}$$

(12)

For isotherms, nonlinear parameter optimization was performed by varying the model parameters while minimizing the R^2 value in order to obtain a better fit of the experimental data than is achieved by linearization.

3. Results and discussion
3.1. Kinetic studies
The effect of initial copper concentration (C_o) on the removal of Cu(II) ions from solution was investigated in the range: 200 mg L^{-1} $\leq C_o \leq$ 500 mg L^{-1} at room temperature. The results are plotted in Fig. 1, and indicate that the obtained curves have the same shape.
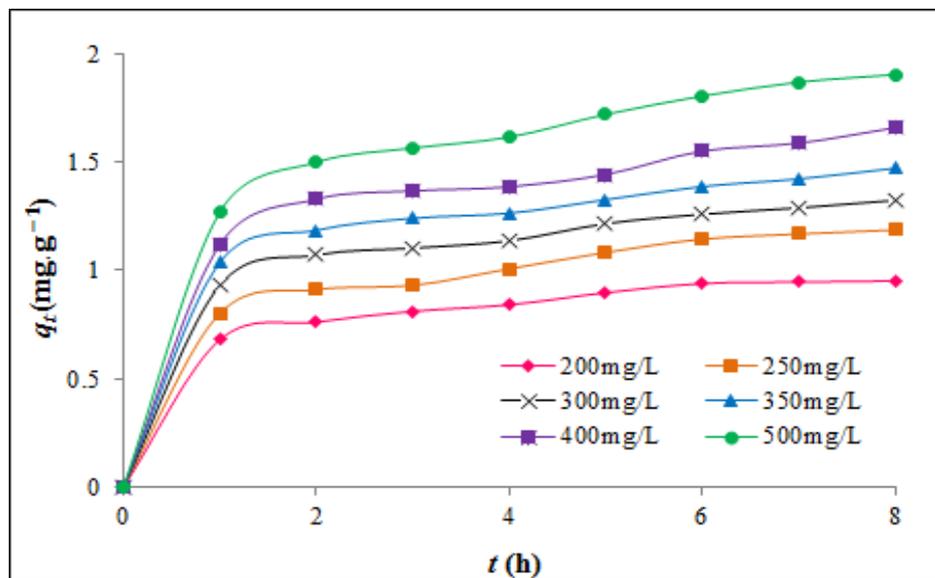
Figure 1: Effect of initial copper concentration on Cu(II) adsorption onto TMS (T: room temperature, m = 0.2 g mL^{-1})

The amount of Cu(II) adsorbed increased with increase in contact time and reached equilibrium in 8 h. The equilibrium time is independent of initial copper concentration. But in the first hour, the initial rate of the adsorption was greater for higher initial copper concentration. We also notice that the capacity of copper removal at the equilibrium increases with the initial copper concentration. This is a result of the increase in the driving force from the concentration gradient [14, 15]. Noeline et al. contributed the increase in adsorption capacity with increasing copper concentration to higher probability of collision between Cu(II) ions and adsorbent surface [16].
In order to analyze the adsorption kinetics of Cu(II) ions, four kinetic models were applied by fitting the obtained experimental data to Eqs (7−11). Figures 2−5 show the obtained linear plots of the four models and Table 1 summarizes the involved kinetic parameters in each model.
The correlation coefficients (R^2) for the Lagergren-first-order kinetic model and for the Elovich equation are lower than that of the pseudo-second order kinetic model. This means that the studied Cu(II) adsorption by TMS are not followed by the Lagergren-first-order kinetic model or Elovich equation, whereas the pseudo-second-order kinetic model is more adequate. In fact, the equilibrium sorption capacities for the second-order correlation are more reasonable when compared with the experimental results than those of the first-order system. The calculated adsorption capacity values ($q_{e,cal}$) agreed perfectly with the experimental ones ($q_{e,exp}$). As

it is listed in Table 1, the pseudo-second-order rate constants decrease from 0.022 to 0.009 g mg^{-1} min^{-1} with the increase of the initial copper concentration (from 200 to 500 mg L^{-1}). On the other hand, the initial sorption rates, h, increase from 0.023 to 0.040 when increasing the initial metal concentrations.
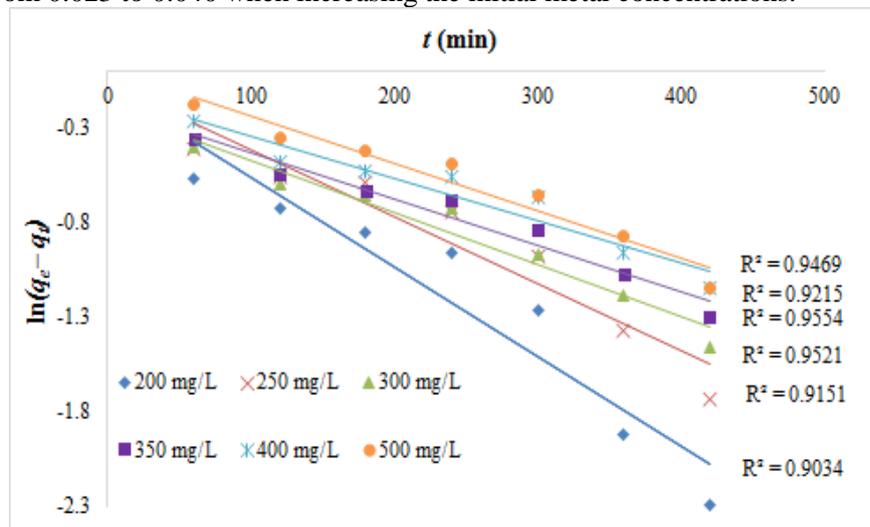
Figure 2: Pseudo-first-order kinetic plots for the adsorption of Cu(II) ions onto TMS for different copper concentrations.
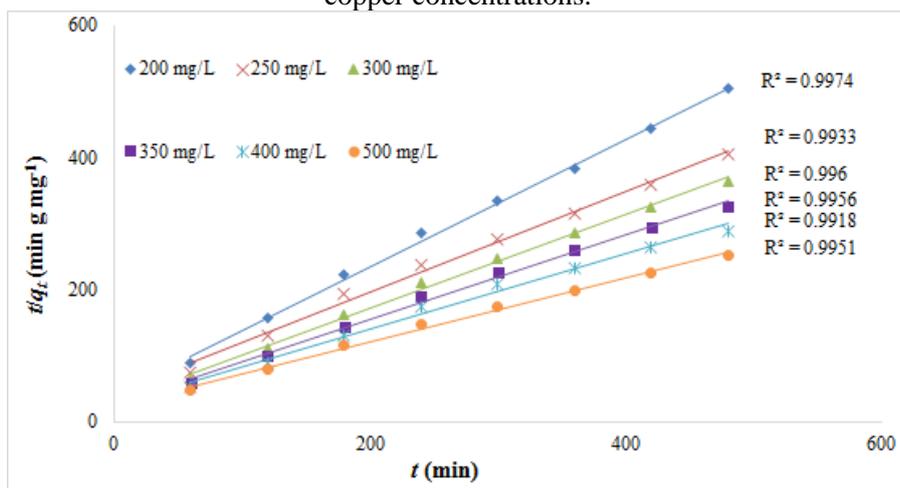
Figure 3: Pseudo-second-order kinetic plots for the adsorption of Cu(II) ions onto TMS for different copper concentrations.
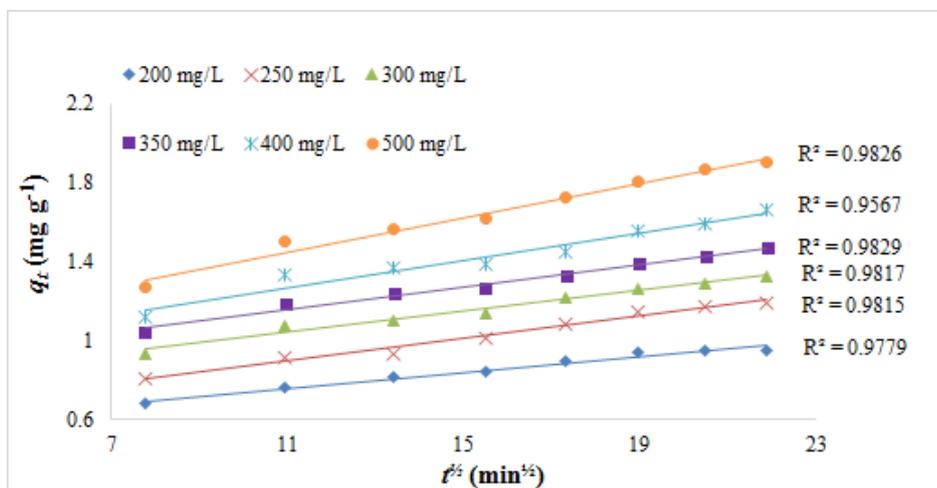
Figure 4: Intraparticle diffusion model plots for the adsorption of Cu(II) ions onto TMS for different copper concentrations.
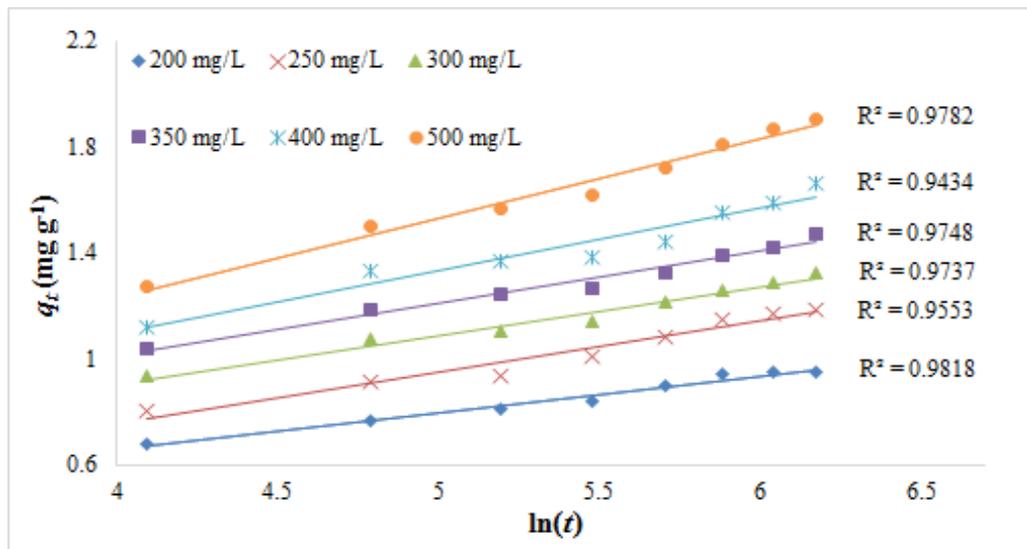
Figure 5: Elovich equation model plots for the adsorption of Cu(II) ions onto TMS for different copper concentrations.

Table 1: Kinetic parameters for Cu(II) adsorption by TMS for different models and different copper concentrations.

Kinetic model	Parameters	C_0 (mg L^{-1})					
		200	250	300	350	400	500
Pseudo-first-order kinetic model	$q_{e,exp}$	0.952	1.187	1.323	1.472	1.659	1.903
	$q_{e,cal}$	0.855	1,020	1.109	1.211	1.352	1,605
	k_1	0.010	0.008	0.006	0.0055	0.0051	0.0058
	R^2	0.903	0.915	0.952	0.955	0.921	0.947
Pseudo-second-order kinetic model	$q_{e,exp}$	0.952	1.187	1.323	1.472	1.659	1.903
	$q_{e,cal}$	0.950	1.172	1.300	1.343	1.603	1.869
	k_2	0.022	0.013	0.016	0.015	0.011	0.009
	h	0.023	0.022	0.032	0.036	0.034	0.040
	R^2	0.997	0.993	0.996	0.996	0.992	0.995
Intraparticle diffusion model	k_i	0.020	0.028	0.027	0.029	0.034	0.043
	C	0.538	0.581	0.746	0.839	0.888	0.972
	R^2	0.978	0.981	0.982	0.983	0.957	0.983
Elovich equation	α	0.290	0.214	0.469	0.603	0.452	0.338
	β	7.215	5.165	5.452	5.058	4.244	3.347
	R^2	0.982	0.955	0.974	0.975	0.943	0.978

The first-order, pseudo-second-order and Elovich models cannot identify the diffusion mechanism and the kinetic results were then subjected to be analyzed by the intraparticle diffusion model. If the diffusion mechanism is the rate-controlling step, then the plot of uptake, q_t, *versus* square root of time, $t^{1/2}$, should be linear and if it passes through the origin then the intraparticle diffusion will be the sole rate-limiting process [17, 18]. Fig.4 shows that q_t =f($t^{1/2}$) plots are linear which do not cross the origin. This indicates that although intraparticle diffusion is involved in the adsorption process, it is not the rate-controlling step. Obtained rate constants, k_i, from the slopes of the straight lines are given in Table 1. From these results, k_i increased with the increase of initial copper concentration. Similar observations were reported for copper by El Ghali et al. [17]. The authors contributed these results to the increase of the driving force for diffusion.

Based on the high correlation coefficient values reported in Table 1, it can be inferred that the Cu(II) adsorption onto TMS followed the pseudo-second-order model than that of the intraparticle diffusion model, Elovich kinetic model and pseudo-first-order model. As a consequence, the rate-limiting step of the Cu(II) adsorption is the chemical adsorption [11, 19, 20].

3.2. Adsorption isotherms
The sorption capacity of adsorbent can be described by equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of the adsorbent [21,22]. The metal uptake as a function of the equilibrium concentration of Cu(II) is presented in Fig. 6. The data show increased uptake with increasing concentration whereby the slope of the curve gradually decreased. Langmuir and Freundlich parameters were obtained both by linear and nonlinear fitting and tabulated in Table 2. The calculated data of Freundlich isotherm which exhibited the highest regression correlation (> 95%) described a better fitting model than that of Langmuir isotherm. The better fitting of the Freundlich isotherm model may be attributed to the heterogeneous distribution of adsorption active sites on TMS surfaces. The adsorption intensity given by the Freundlich coefficient ($1/n$) is smaller than 1 indicating that the adsorption of Cu(II) onto TMS samples under studied conditions is favorable.

From Table 2, it can be observed that the values of K_L and q_{max} constants obtained by nonlinear regression are different from those of the linear transform. Although these results can be reasonable by the fact that multiple optimum may exist. However, one can notice that the coefficient of determination of Langmuir is lower than that of Freundlich. In addition, similar constants of Freundlich isotherm were obtained for the linear and nonlinear regression with coefficients of determination greater than 95%. It can be then inferred that the Freundlich model gives the best approximation to the optimum parameter set obtained by nonlinear regression. This suggested that sorption modeling of Cu(II) onto TMS is better described by Freundlich isotherm than by Langmuir isotherm. The same discussion was reported by Schiewer and Balaria [23].
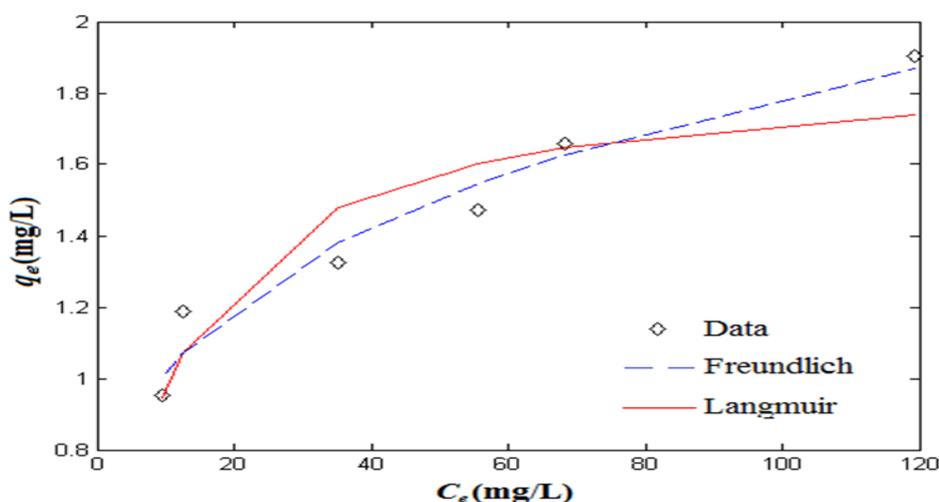
Figure 6: Equilibrium curves for sorption of Cu(II) onto TMS using nonlinear parameter optimization (T: room temperature, pH = 4, m = 0.2 g mL^{-1}).

Table 2: Equilibrium parameters for Langmuir and Freundlich isotherm models.

Isotherm	Type	Model parameter		R^2
Langmuir	Linear	$K_L = 0.068$	$q_{max} = 2.059$	0.826
	Nonlinear	$K_L = 0.105$	$q_{max} = 1.877$	0.876
Freundlich	Linear	$K_F = 0.582$	$1/n = 0.242$	0.954
	Nonlinear	$K_F = 0.571$	$1/n = 0.248$	0.955

3.3. Desorption and regeneration studies
In order to make the adsorption process more economically, it is important to desorb and reuse the spent adsorbent. Metal sorbed can be desorbed by a suitable eluent or desorbing solution, and thus the adsorbent can

be used in multiple sorption–desorption cycles. The desorption studies were carried out by batch process using distilled water, HCl, HNO$_3$, CH$_3$COOH, NaCl, Na$_2$SO$_4$ and EDTA being the concentrations of all acids and salts 0.1 M. Figure 7 shows the percentage of Cu(II) released after treatment with these different desorbents. As found, EDTA and HCl were the most efficient eluents.
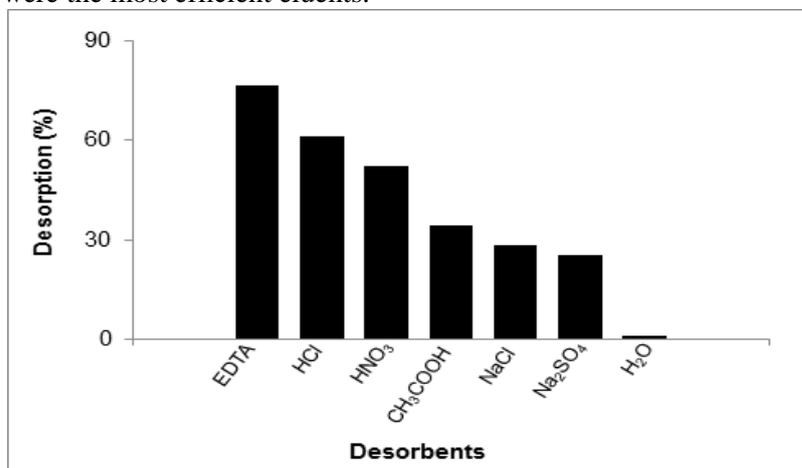
Figure 7: Cu(II) recovery from TMS-Cu by different desorbents.

The reuse of loaded TMS adsorbent was examined using adsorption/desorption cycles. Figure 8 shows the amount of copper sorbed and desorbed in each cycle. The results indicate that in 3 cycles, adsorption decreases from 93 to 68 %, while the recovery of Cu(II) decreases from 61 to 40 % after three regeneration cycles. Similar results were reported in the literature [24,25]. The reduction of Cu(II) adsorption percent in the first regeneration cycle may be attributed partly to certain adsorption sites of functional groups that are decomposed or destroyed by the hydrochloric acid, or/and to complexation of copper by chloride ion. The results in Fig. 8 show that the amount of metal ions sorbed after the first sorption/desorption cycle process are almost the same indicating that the adsorbent TMS can be recyclable.
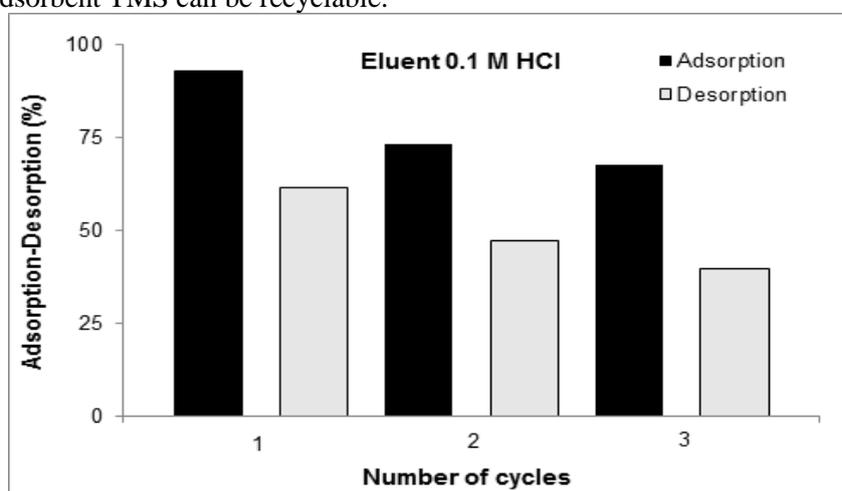
Figure 8: The performance of TMS by multiple cycles of regeneration.

Conclusions
1. The present study investigated the effectiveness of treated Martil sand (TMS) in the removal of copper.
2. The equilibrium time is independent of initial copper concentration.
3. The adsorption capacity increases with increase in metal ion concentration.
4. The adsorption kinetic data were fitted better to the pseudo-second-order kinetic model than the intraparticle diffusion, Elovich kinetic and pseudo-first-order models.
5. Equilibrium adsorption data were better described by the Freundlich adsorption model.
6. Cu-loaded TMS was successfully regenerated using EDTA and HCl and reused for three cycles.
7. Overall this study suggested that the adsorption of Cu(II) by TMS can be an inexpensive and effective way for metal ion treatment and should be investigated further for its practical application.

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(2015); http://www.jmaterenvironsci.com