

Kinetics of copper (II) Adsorption by Bentonite in Mixed Solvents

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Abstract: Bentonite clays are known for their industrial importance. Kinetics and mechanism of Cu(II) ions adsorption on local bentonite have been studied. The effect of Cu(II) ion concentration, solvents, and mixing rates were investigated. Adsorption measurements showed that the process is very fast and physical in nature. The initial Cu(II) concentration, mixing rate and solvent type affected the rate of the adsorption reaction. Data were modeled using first and second order kinetic equations, mass transfer, and intra-particle diffusion models. The second order kinetic equation showed to best describe the sorption kinetics. Furthermore, the adsorption from water and methanol-water follow Freundlich and from acetone-water follows Langmuir isotherms. The adsorption mechanism did not fit the mass transfer nor intra-particle diffusion models, indicating that Cu(II) is exchanged by cations on the bentonite surface.

Introduction

Copper is a transitional metal with three common oxidation states: Cu⁰ (metal), Cu⁺ (cuprous ion), Cu²⁺ (cupric ion). Cupric ion is the most commonly occurring species, which readily forms free hydrated ions in water, it prevails in the environment and is the most toxic to living organisms among the three species. Toxicity of copper to living organisms is essentially exerted on enzymes, especially those whose activities depend on sulfhydryl and amino groups, because copper, a soft acid, has a high affinity for ligands containing nitrogen and sulfur donors (Sharma Y. and Weng C., 2007). Potential sources of toxic copper metal ions are, essentially, the industrial waste streams of metal cleaning and plating baths, pulp, paper, paperboard and wood preservative-employing mills, the fertilizer industry, etc. (Gundog R. et. al., 2004).

There are several methods to treat the metal contaminated effluent such as precipitation, ion exchange, adsorption, etc., but the selection of the wastewater treatment method is based on the concentration of waste and the cost of treatment. Adsorption is one of the most popular methods for the removal of heavy metals. In the purification process, low cost purificant-adsorbent systems are preferred (Wang S., and Wu H., 2006; Omer Y. et. al., 2003). For this reason, industrial wastes and metallurgical by-products are used as well as natural substances like activated carbon and clay minerals [5-10]. (Weng

C. et. al., 2007; Khazali O. et. al., 2007 ; Weng C. and Pan Y., 2006; Ajmal M. et. al., 2003; Machida M. et. al., 2005; Bulut Y., and Baysal Z., 2006). Activated carbon is among the most effective adsorbents, having high surface area per unit mass and exhibits high adsorption capacity for heavy metals (Kadirvelu K. et. al., 2001; Hasar H., 2003). The relatively high cost of activated carbon encouraged attempts to utilize low cost, naturally occurring adsorbents to remove trace organic and inorganic contaminants from wastewaters (Hu C., and Xia M., 2006).

There has been increasing interest in utilizing natural clay minerals like montmorillonite, kaolinite, and illite for the removal of toxic metals and some organic pollutant from aqueous solutions (Veli S. and Alyüz B., 2007; Plecas I. et. al., 2004; Kaya A. and Hakan A., 2005; Stathi P. et. al., 2007). Bentonite consists essentially of clay minerals of the smectite (montmorillonite) group and has a wide range of industrial applications including clarification of edible and mineral oils, paints, cosmetics, and pharmaceuticals (Christidis G., 1998). The abundance of bentonite in most continents of the world and its low cost make it a strong candidate as an adsorbent for the removal of many pollutants from wastewaters. Many studies were carried out to investigate the possible use of natural bentonite as an effective adsorbent for the removal of rare earth elements and heavy metals from aqueous solutions (Mellah A. et. al., 2006). It was found (Al-Qunaibit M. et. al., 2005) that the untreated clay has higher affinity for heavy

metals than the treated.

Using bentonite for heavy metal sequestering from solvents other than water is still rather limited, therefore the aim of this work is to study the kinetics of removal of Cu(II) by adsorption on a Saudi natural bentonite in aqueous and mixed-solvent metal solutions. We investigated the adsorption of Cu(II) on bentonite in water and two mixed solvent systems, (water + methanol, 50 % v/v) and (water + acetone, 50 %v/v) which, to our knowledge, have not been studied to date. These solvents differ in their polarity and acidic properties, and thus expected to have a pronounced influence on the adsorption of Cu(II) on bentonite surface .

Materials and Methods

Materials and instrumentation

The bentonite used in this study was generously supplied by The Saudi Ceramic Company (clay location: north Jeddah, K. Saudi Arabia). Acetone and methanol used were of analytical reagent grade (BDH, England). Cu(II) stock solutions were diluted from a 10g/l analytical grade sulfate solution (WTW). Deionized water was used for preparing all solutions. In order to maintain the cost effectiveness of the process, bentonite was used in the experiments without any pretreatment with a mean particle size of 60 μm . Changes in metal ion concentration in solution were followed using a WTW pM X 3000 microprocessor-controlled high-performance pH ion meter using a solid state Cu(II) ion selective electrode. The instrument was calibrated periodically in terms of concentration using a set of Cu(II) standard solutions. All experiments were conducted at ambient temperature.

Kinetic procedure

Kinetic runs were started by the addition of a weighted air-dried bentonite sample (0.1g) to polyethylene cups each containing 50 ml of Cu(II) solution in water or in acetone-water or methanol-water, with continuous stirring at 200 rpm. One ml of 5 M NaNO_3 was added to operate at constant ionic strength. Kinetic runs were carried out using three different initial concentrations of Cu(II): 50, 70, and 100 mg/l for each system. In this method, the dried clay sample was added very rapidly to the stirring Cu(II) solution. As the copper ions are adsorbed by the bentonite sample, their concentration in the

suspension decreased, causing a change in the emf of the Cu(II) ion-specific electrode. A continuous record of Cu(II) ion concentrations versus time was obtained at time intervals of 30s and up to 900s using a strip chart.

Sorption experiments

Sorption isotherm studies were conducted in 100ml closed polyethylene bottles. Each bottle contained 50 ml of Cu(II) solution with concentrations ranging from 10 to 100 mg/l, and 0.1g of bentonite. Following a 24-h reaction period on a mini shaker, the copper ions concentration in each bentonite suspension was recorded. Solid-phase loading of Cu(II) concentration, q_e (mg/g) was computed from the mass balance: $q_e = (C_0 - C_e)/M$, where C_0 and C_e are the total dissolved and equilibrium liquid phase Cu(II) concentration (mg/l), respectively, and M is the dose of bentonite (g/l).

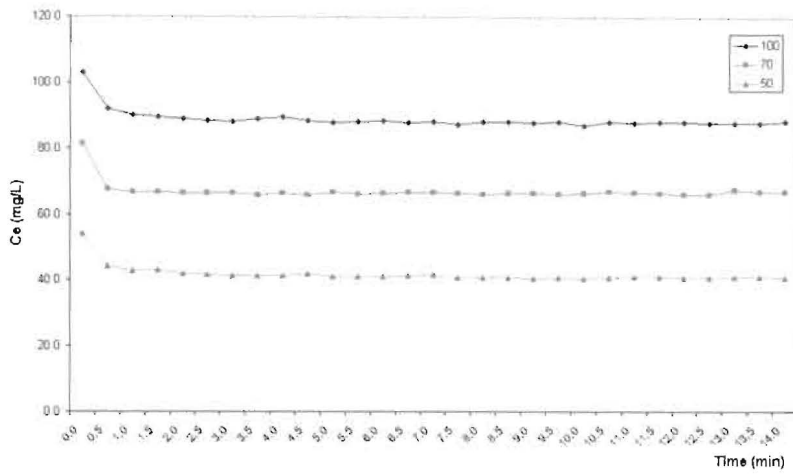
Mixing rate experiments

The decrease in Cu(II) concentration with time using 100 mg/l aqueous, methanol-water and acetone-water solutions was recorded at two mixing rates; 200 and 350 rpm.

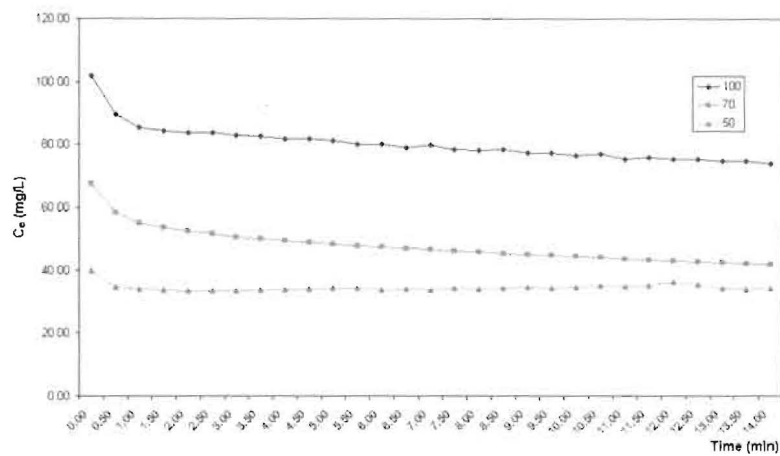
Results and Discussion

Effect of contact time and concentration on removal of Cu(II)

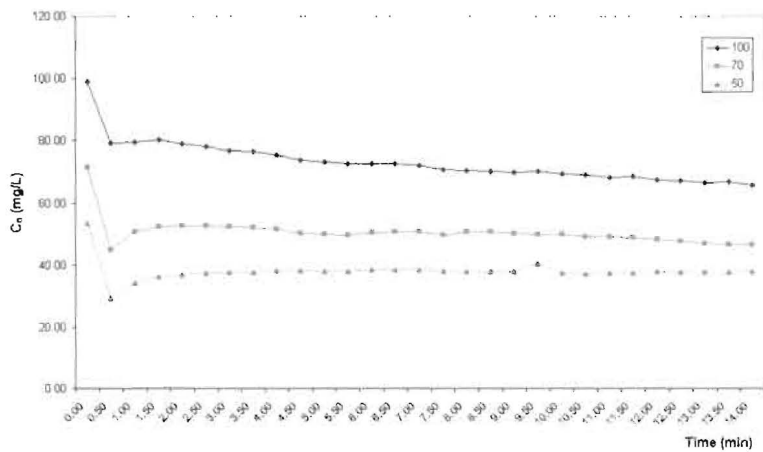
Two factors affect the adsorption process: (a) the initial concentration of the adsorbate in solution, (b) and time of contact between adsorbate and adsorbent phases. During the removal of Cu (II) ions by adsorption on bentonite, the concentration of Cu(II) ions in solution decreases with increasing time and reaches a minimum value within 5 min, and thereafter it remains constant in water or methanol-water and acetone-water (Fig.1 a ,b and c). The curves obtained are single and smooth indicating formation of monolayer on the surface of the adsorbent during removal process. In initial stages, the slope of the plots is greater and it decreases with time. It reveals that the rate of uptake is rapid in early stages and gradually decreases and becomes constant when the equilibrium is attained. The time required to attain equilibrium is relatively longer in water-methanol or water-acetone than in aqueous solution. Similar results were reported by some researchers for a variety of adsorbate-adsorbent systems (Panday K. et. al., 1985; Acemiolu B. and Alma M., 2001).



1 (a)



1(b)



1 (c)

Fig. 1. Effect of initial adsorbate concentration on the adsorption of Cu(II) onto bentonite in different solvents: (a) water ,(b) methanol-water and (c) acetone-water at different Cu(II) concentrations

Kinetics and Mechanism

Several models have been proposed to express the mechanism of solute molecule adsorption onto an adsorbent: (a) pseudo-first-order kinetics model, (b) pseudo-second-order kinetic model, (c) intra-particle diffusion model (Weber W., and Morris J., 1963) and (d) a mass transfer model (Furusawa T., and Smith J., 1974).

A pseudo-first-order kinetic model of Lagergen is given as :

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where q_t is the amount of Cu (II) sorbed (mg/g) at time t (min), q_e is the amount of Cu(II) sorbed at equilibrium (mg/g) and k_1 is the Lagergen rate constant of adsorption (min^{-1}) for the pseudo-first-order model. Plots of $\log(q_e - q_t)$ versus t were drawn at different initial concentrations and different solvents (not shown). From linear regression analysis, it was determined that R^2 values were very low for any Cu(II) concentration and solution system, indicating that the adsorption of Cu(II) from water, methanol-water and acetone-water do not fit the proposed first-order model. Values of rate constants (k_1) and R^2 are presented in Table 1.

A pseudo-second-order kinetic model of Ho (Ho Y., 2004) is:

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

where k_2 is the rate constant for the pseudo-second-order model, q_e and q_t are the amount of solute adsorbed per unit adsorbent at equilibrium and at any time, respectively. Herein, the initial adsorption rate is $h = k_2 q_e^2$.

Linear plots of t/q_t versus t were obtained at different initial concentrations and solvents as shown in Fig.2. This figure indicates that pseudo-second order rate equation yields the best fit and correlation coefficients (R^2) are close to unity for the three systems, suggesting that kinetics of Cu(II) adsorption by Saudi bentonite can be described by this model. The values of equilibrium capacity (q_e), pseudo second-order rate constant k_2 and initial adsorption rates (h) for the adsorption of Cu(II) ions onto the bentonite were calculated from the slopes and intercepts of the plots in Fig.2. The data obtained are presented in Table 2.

If we took into consideration that the lower the initial concentration of copper, the higher the error in concentration determination when employing such a sensitive technique (potentiometry), accordingly looking only at results of 100 mg/l solutions in all solvents, a general trend in adsorption can be concluded for the three systems: Cu(II) amount adsorbed increases with increasing

Table 1. Pseudo first-order model parameters

Solvent	K_1			R^2		
	50mg/l	70mg/l	100 mg/l	50mg/l	70mg/l	100 mg/l
Water						
Methanol-water	-0.03	-0.01	-0.03	0.38	0.08	0.34
Acetone-water	0.01	-0.02	-0.02	0.44	0.88	0.84
	00	-0.01	-0.02	00	0.64	0.83

Table 2 . Pseudo second-order kinetics parameters

	Water			Water-methanol			Water-acetone		
	50mg/l	70mg/l	100mg/l	50mg/l	70mg/l	100mg/l	50mg/l	70mg/l	100mg/l
q_e (mg/g)	6.6	7.2	7.6	2.85	12	12.77	7.88	13.6	18.5
$h=k_2 q_e^2$	42	79	55	4	9	11	455	16	12
k_2	0.96	1.52	0.95	0.49	0.06	0.06	7.32	0.08	0.03
R^2	0.99	0.99	0.99	0.93	0.98	0.99	0.99	0.99	0.99

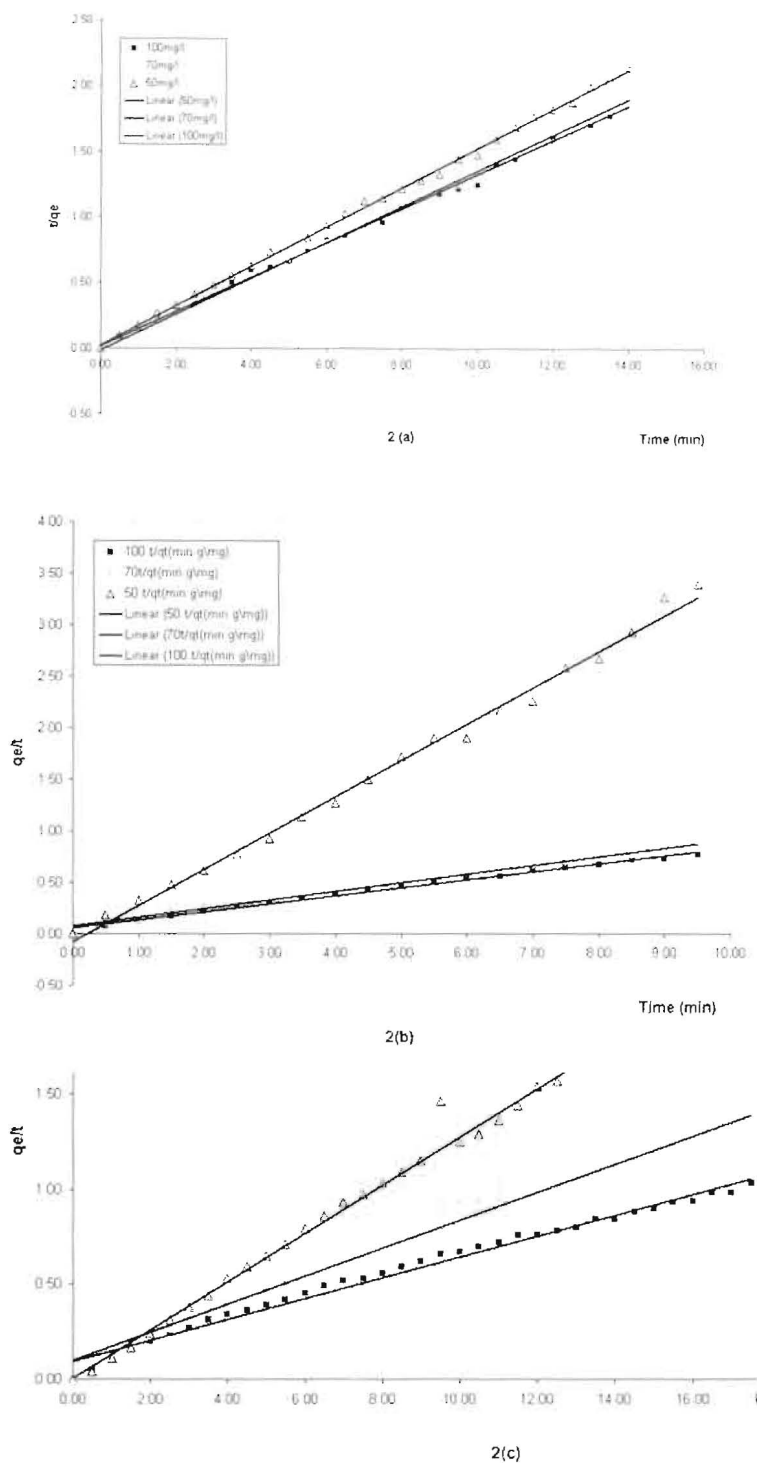


Fig. 2. Pseudo second-order kinetics of Cu(II) adsorption onto bentonite at various initial concentrations in (a) aqueous solution, (b)methanol-water and (c) acetone-water.

copper concentration and with decreasing polarity of solvent. At the same time, the second-order rate constants (k_2), decreased by decreasing polarity of solvent but it remains nearly constant with increasing Cu(II). The results of the present study are in accord with those reported by Ho and McKay for the adsorption of dye onto peat (Ho Y. and McKay G., 1999) and by Gündoan et al for adsorption of Cu(II) onto peat (Gundog R. et. al., 2004).

An intra-particle diffusion model of Weber (Weber W., and Morris J., 1963), equation 3, and model of mass transfer of solid from the aqueous phase onto the solid surface (Furusawa T. and Smith J., 1974), equation 4, have been used for the present investigations.

$$q_t = k_i t^{1/2} \quad (3)$$

where k_i is the intra-particle diffusion rate constant,

$$\ln \left[\frac{C_t}{C_0} - \frac{1}{1+mk} \right] = \ln \left[\frac{mk}{1+mk} - \frac{1+mk}{mk} \right] \beta_1 S_s t \quad (4)$$

where m (g l^{-1}) and S_s (cm^{-1}) are the mass and outer surface of the adsorbent particles per unit volume of particle-free slurry, respectively, k (l g^{-1}) is a constant known as Langmuir's constant and β_1 (cm s^{-1}) is the mass transfer coefficient. The values of m and S_s were calculated using the following relations:

$$m = \frac{W}{V} \quad (5)$$

$$S_s = \frac{6m}{d_p \rho_p (1 - \epsilon_p)} \quad (6)$$

where W (g) is the weight of the adsorbent, V (l) the volume of particle-free slurry solution, and d_p (cm), ρ_p (g cm^{-3}) and ϵ_p are the diameter, density and porosity of the adsorbent particles, respectively.

Plots of q_t versus $t^{1/2}$ for the intra-particle diffusion model were obtained at different initial concentrations and solvent mixtures, but are not demonstrated due to their low correlation coefficients. Plots of $\ln \left[\left\{ \frac{C_t}{C_0} - \frac{1}{1+mk} \right\} \right]$ versus t does not fit with the proposed model for Cu (II) adsorption on bentonite. Hence, from the above results, it was concluded that the Cu(II) adsorption is not compatible with intra-particle diffusion nor mass transfer models. The bentonite used in this study was untreated, therefore it has many cations and organic

materials on the surface, and a reaction between functional groups of organic and inorganic matter at the bentonite surface and copper ions is expected. In particular, exchangeable cations such as Ca^{2+} , Mg^{2+} , H^+ , Na^+ , and K^+ in bentonite can allow Cu(II) adsorption via cation-exchange mechanism (El-Batouti M. et. al., 2003). Therefore, in this study, it is proposed that the mechanism of Cu(II) adsorption onto the Saudi bentonite investigated is a cation-exchange mechanism.

Adsorption isotherms

Fig.3 shows the adsorption isotherms of Cu(II) onto bentonite in aqueous, methanol-water, and acetone-water solutions as a function of time at room temperature. The isotherms indicate that complete saturation of Cu(II) ions on the bentonite's surface is not attained in case of adsorption from water nor from mixed solvent systems under investigation. The adsorption potential of Cu(II) from the acetone-water mixture was greater than from methanol-water and that from water. This phenomenon could be attributed to the interaction of Cu(II) with both solvent and sorbent. Cu(II) is known to have good solubility in water (24.3g/100ml at 0°C and 205g/100ml at 100°C) resulting from bonding between water and Cu(II) (Francis C., 1987), which is promoted by the dipole moment (1.8 D) of water (for methanol 1.7D and for acetone 2.7D), therefore acetone-water system exhibits less tendency for interaction with Cu(II). Cation exchange in mixed solvents has been studied and it was found (El-Batouti M. et. al., 2003; Samuelson O., 1963) that the selectivity coefficient for an ion is usually greater in solvents with lower dielectric constants than water.

Because of the low polarity of acetone, its interaction with Cu (II) is weak and the solubility of the divalent ion is limited relative to that in water or methanol. To achieve adsorption, the interaction between Cu(II) and bentonite should be stronger than that between copper ions and the solvent. This is manifested in the results of the current study and is in accord with the findings of M. El-Batouti (El-Batouti M. et. al., 2003) that Cu(II) adsorption from acetone solution occurred preferentially. Bearing in mind that the solvent composition onto the bentonite surface may differ considerably from that in the solution bulk, it can be predicted that the relative solvent composition must also affect the penetration of electrolyte into the bentonite. Generally, an increased penetration of Cu(II) ions is expected when a less

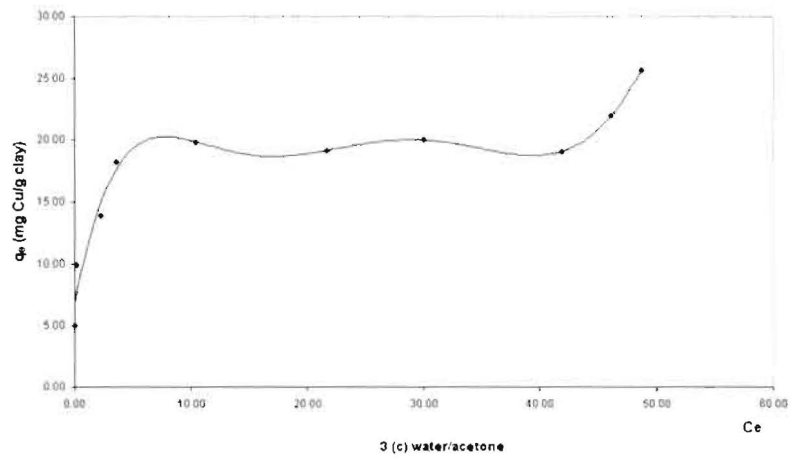
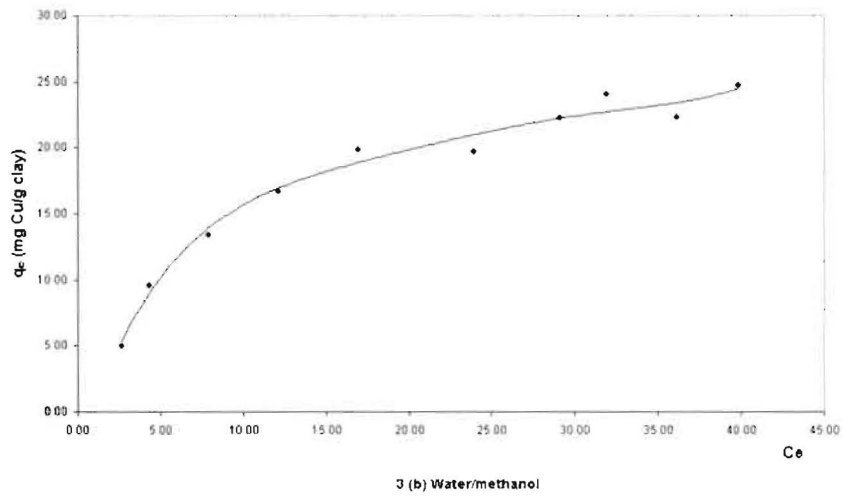
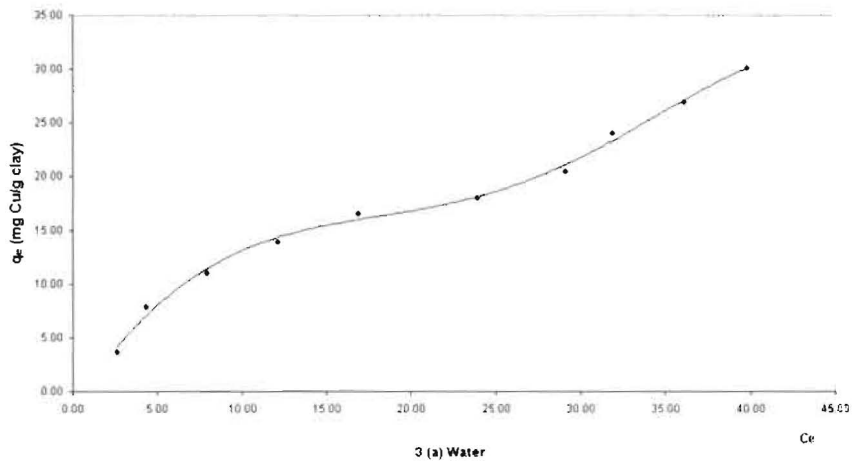
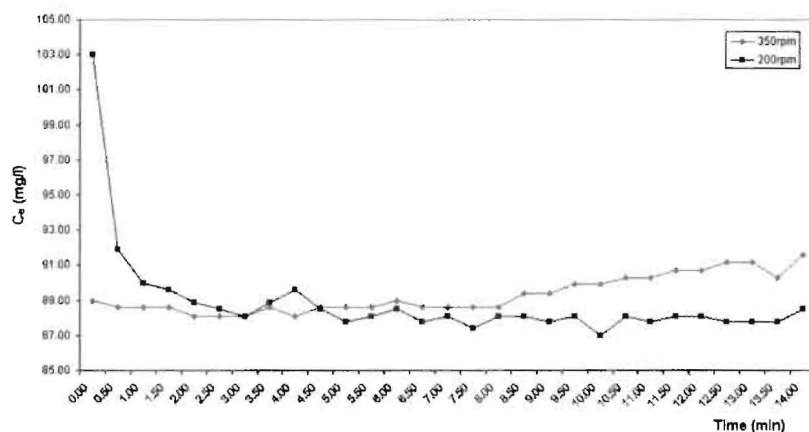
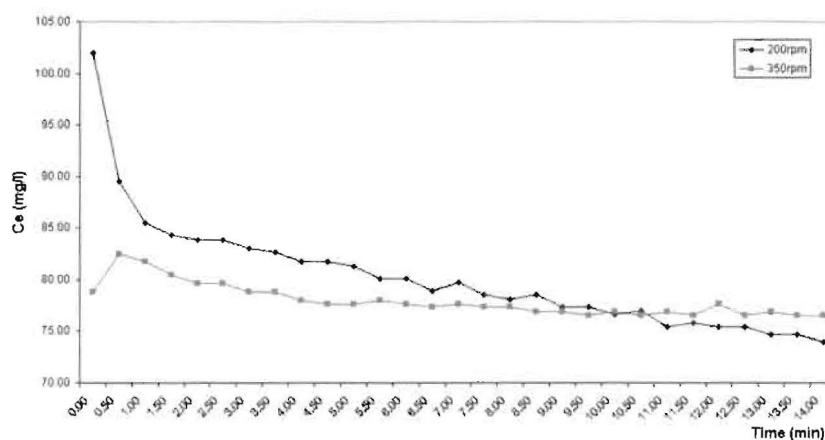


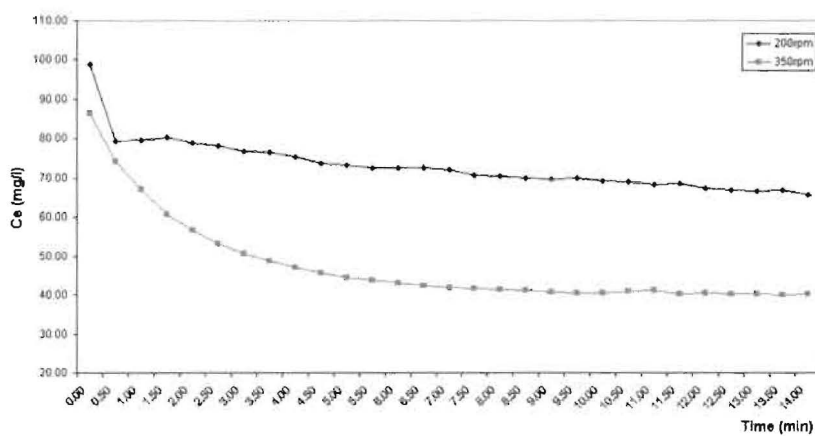
Fig. 3 Adsorption isotherms of Cu(II) onto bentonite in different solvents.



4 (a) Water



4 (b) Water-methanol



(c) Water-acetone

Fig.4 the effect of mixing rate on the adsorption of Cu(II) from 100 mg/l solution.

Table 3. Freundlich and Langmuir constants

Solvent	Freundlich constants			Langmuir constants		
	k (mg/g)	n (g/l)	R ²	a	b (mg/g)	R ²
water	2.48	1.51	0.97	-	-	-
water/methanol	19.99	1.46	0.93	-	-	-
water/acetone	-	-	-	0.72	22.47	0.97

polar solvent is added to bentonite in equilibrium with a water solution.

Experimental data for adsorption of Cu(II) from water and methanol-water were best fitted to the Freundlich equation, while the adsorption of Cu(II) from acetone-water system onto bentonite was best fitted to Langmuir (table 3).

The Freundlich isotherm is expressed as:

$$\ln q_e = \ln k + 1/n \ln C_e \quad (5)$$

where (q_e) is the amount of metal ions adsorbed per unit weight of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of metal ions, and k (mg g^{-1}) and n (g l^{-1}) are Freundlich constants, which are the adsorption capacity of the adsorbent and the indication of the favorability of the adsorption process, respectively. The values of k and n were calculated from the slope and intercept of the plots of $\ln q_e$ versus $\ln C_e$.

The rearranged Langmuir expression is:

$$\text{or } C_e/q_e = 1/ab + C_e/b \quad (6)$$

Where (a) is the affinity constant and (b) is the maximum amount adsorbed (mg/g) and are determined from the slope and intercept of the plots of C_e/q_e against C_e .

The values obtained from the Freundlich and Langmuir isotherms are presented in Table 3.

Mixing rate effect

As seen from Fig.4 a, b and c, the increase in mixing rate seems to affect the sensibility of the electrode even before adding the clay. As the experiment proceeds copper concentration decreases but increases again in aqueous and water-methanol solutions at 350 rpm, while decreases appreciably in the acetone-water solution at the same rate which confirms the different nature of Cu(II) bonding in this solvent. As acetone is of low polarity, it will not be attracted to the charged surface functional groups. Therefore, it diffuses between the silicate sheets of

the bentonite particles weakening the attraction forces between binding silicate sheets in a crystalline structure and, consequently, converts it to an amorphous form. This results in a substantial increase in the surface area of bentonite which results in high adsorption capacity of bentonite for Cu(II)

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