

# Study of Cu(II) biosorption by dried activated sludge: effect of physico-chemical environment and kinetics study

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## Abstract

Biosorption is a recent technology used to remove heavy metal ions from aqueous solutions. The biosorption of copper ions from aqueous solution by dried activated sludge was investigated in batch systems. Effect of solution pH, initial metal concentration and particle size range were determined. The suitable pH and temperature for studied conditions were determined as 4.0 and 20 °C, respectively. The theoretical max biosorption capacity of activated sludge was 294 mg g<sup>-1</sup> at 20 °C for <0.063 mm particle size. The equilibrium data fitted very well to both Langmuir and Freundlich isotherm models. The pseudo first and second-order kinetic models were used to describe the kinetic data. The experimental data fitted to second-order kinetic model. The particle size and initial metal concentration were effected the biosorption capacity of dried activated sludge. An increase in the initial metal concentration increases of biosorption capacity, which also increases with decreasing particle size. Dried activated sludge has different functional groups according to the FT-IR results.

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## 1. Introduction

Toxic heavy metal containing industrial wastewater can cause serious environmental pollution problems for aquatic life. The removal of toxic contaminants and organic pollutants from industrial wastewaters is one of the most important environmental issues. The main industrial sources of toxic metal contamination in wastewaters include electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing industries, etc. Some heavy metals are necessary in small amounts for normal development of biological cycles; however most of these heavy metals are becoming toxic at high concentrations [1].

Many physico-chemical methods have been developed for heavy metal removal from aqueous solution, including

chemical coagulation, evaporation, adsorption, extraction, ion-exchange and membrane separation process [2,3]. Among these methods, ion-exchange is a highly popular one and has been widely practiced in industrial wastewater treatment process. But the application of such processes is often restricted because they cannot guarantee the metal concentration limits required by regulatory standards as they produce wastes difficult to treat, either they can cause very expensive costs, especially when metal concentrations in the effluents are below 100 mg L<sup>-1</sup> [4,5].

Adsorption is a well-established technique for heavy metal removal. Activated carbon is a widely used adsorbent material. In fact use of activated carbon can be expensive due to the regeneration required and loses in the application processes. Many investigators have studied inexpensive alternative materials instead of activated carbon for removal of heavy metal from wastewaters. Some of the these alternative adsorbent materials are algae [6], almond husk [7], clays [8], yeast biomass [9], perlite [10], maple sawdust

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### Nomenclature

$a_L$ and $K_L$	Langmuir isotherm constants
$C_0$	initial metal concentration ( $\text{mg L}^{-1}$ )
$C_e$	equilibrium metal concentration in solution ( $\text{mg L}^{-1}$ )
$C_t$	equilibrium metal concentration in solution at time $t$ ( $\text{mg L}^{-1}$ )
$h$	initial sorption rate
$k_i$	intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{0.5}$ )
$K_1$	pseudo first-order rate constant ( $\text{min}^{-1}$ )
$K_2$	pseudo second-order rate constant ( $\text{g mg}^{-1} \text{min}$ )
$K_F$	Freundlich isotherm constants ( $\text{L g}^{-1}$ )
$n$	exponent in Freundlich equation dimensionless
$N$	the number of measurements
$P_s$	particle size (mm)
$q_e$	equilibrium metal concentration on biomass ( $\text{mg g}^{-1}$ )
$q_{e \text{ cal}}$ and $q_{e \text{ exp}}$	experimental and calculated values of $q_e$ ( $\text{mg g}^{-1}$ )
$q_{\text{max}}$	maximum monolayer capacity ( $\text{mg g}^{-1}$ )
$q_t$	adsorbed metal concentration at time $t$ ( $\text{mg g}^{-1}$ )
$r^2$	correlation coefficients
$R_L$	dimensional separation factor
S.D.	standard deviation
$V$	solution volume (L)
$W$	adsorbent weight (g)
$\varepsilon$ (%)	average percentage errors

[11], seaweeds [12], pine bark [13], fly ash [14], etc. for the removal of heavy metal from wastewater. Activated sludge process, the most common used biological wastewater treatment method, is the most abundant source of microbial biomass. There have been many investigations on the use of activated sludge biomass to remove and accumulate heavy metals [15,16]. Non-living biomass is generally used for biosorption studies. It eliminates the problem of heavy metal toxicity and different factors [17,18].

Industrial wastes are important pollutants for the feature of terrestrial and aquatic life. Toxic metal contamination in wastewaters is unwanted for continuity wastewater treatment system and aquatic life. Removal of heavy metal from wastewater is expensive. Biosorption technique is known as an effective method for removal of pollutants from aqueous solutions. In this paper, FT-IR characterization of dried activated sludge and Cu(II) ions biosorption properties were determined in batch adsorption system and the effect of some physico-chemical parameters on biosorption of Cu(II) ions were investigated such as particle size range of dried

activated sludge, initial Cu(II) concentration, solution pH and temperature.

#### 1.1. Adsorption isotherms

The adsorption isotherms generally used for the design of adsorption system. The Langmuir [19] and Freundlich [20] equations are commonly used for describing the adsorption isotherm. The linear equation of Langmuir and Freundlich are represented as follows Eqs. (1) and (2), respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left( \frac{a_L}{K_L} \right) C_e \quad (1)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (2)$$

where  $a_L$  and  $K_L$  are the Langmuir isotherm constant;  $K_F$  the Freundlich constant and  $n$  the Freundlich exponent. The ratio of  $K_L/a_L$  gives the theoretical monolayer saturation capacity of dried activated sludge ( $q_{\text{max}}$ ).

The essential characteristic of the Langmuir equation can be expressed in terms of dimension factor  $R_L$ , which was defined by Hall et al. [21], as:

$$R_L = \frac{1}{1 + a_L C_0} \quad (3)$$

where  $a_L$  is the Langmuir isotherm constant and  $C_0$  the highest initial Cu(II) concentration ( $\text{mg L}^{-1}$ ). The value of  $R_L$  indicates the shape of the isotherms to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

#### 1.2. Kinetic modeling

The pseudo first-order model [22], pseudo second-order model [23] and intraparticle diffusion model [24] were used to fit the experimental data.

The pseudo first-order model of Lagergren is given as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (4)$$

The pseudo second-order model is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (5)$$

The initial sorption rate ( $h$ ) is given as:

$$h = k_2 q e^2 \quad (6)$$

The intraparticle diffusion equation can be described as:

$$q_t = k_i t^{0.5} \quad (7)$$

where  $K_1$  is the rate constant of pseudo first-order adsorption ( $\text{min}^{-1}$ ),  $K_2$  ( $\text{g mg}^{-1} \text{min}$ ) the rate constant of pseudo-second order adsorption,  $k_i$  the intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{0.5}$ ).  $q_e$  and  $q_t$  are the amount of adsorbed Cu(II)

concentrations on adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively.

## 2. Experimental

### 2.1. Preparation of adsorbent and adsorbate

Activated sludge biomass, as an adsorbent, was collected from Adana Organize Sanayi biological wastewater treatment system, Adana, Turkey. Activated sludge biomass was harvested by centrifugation and washed twice with distilled water and then was dried at  $60^\circ\text{C}$  until constant weight. Dried activated sludge was broken into pieces and was separated into certain particle sizes by a sieve. Analytical grade  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was used as an adsorbate. The stock solution of Cu(II) was prepared by dissolving in distilled water ( $500$  and  $1000 \text{ mg L}^{-1}$ ). The pH of the Cu(II) solutions was adjusted to  $4.0 \pm 0.1$  by using dilute NaOH or  $\text{H}_2\text{SO}_4$ .

### 2.2. Characterization of activated sludge

Divalent cations on activated sludge biomass and general properties of activated sludge were determined according to standard methods [25]. The FT-IR analysis of activated sludge was determined as follows: KBr pellet was prepared. The proportion of activated sludge biomass/KBr is 1/100. Perkin-Elmer spectrum RX/FT-IR system was used for FT-IR analysis of dried activated sludge.

### 2.3. Biosorption studies

The biosorption of Cu(II) on dried activated sludge was studied by batch technique. Biosorption studies were conducted in 250 mL screw top flasks using 100 mL of biomass–metal solutions. The general method used for this study is described as follows: a known weight of dried activated sludge biomass (0.1 g) was contacted with 80 mL of distilled water before contacting of Cu(II) solution. After than 20 mL known concentration of Cu(II) solution was contacted with biomass-distilled water solution. The solution pH was controlled during the biosorption experiments and pH values were adjusted by using 0.1 M NaOH or  $\text{H}_2\text{SO}_4$  solutions. The flasks were agitated on a shaker at 150 rpm for 420 min. The contact time and biomass concentration was determined with respect to preliminary experiments.

The varying particle size group dried activated sludge were used for effect of particle size on Cu(II) removal. They were  $<0.063$ ,  $0.63$ – $1.25$  and  $1.25$ – $2.50$  mm. Effect of initial Cu(II) concentration on biosorption was investigated at  $100$ – $400 \text{ mg L}^{-1}$  initial metal concentrations. Effects of pH and temperature on biosorption were studied at pH values of 2–6 and temperatures of  $20$  to  $50 \pm 1.5^\circ\text{C}$  at  $100 \text{ mg L}^{-1}$  initial metal concentration and 60 min.

### 2.4. Analysis of metal ions

The concentrations of unadsorbed Cu(II) in the metal–biomass suspension were determined using Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer with air-acetylene flame. A volume of 5 mL biomass–metal suspension was centrifuged at 10,000 rpm (10 min) for removal of activated sludge particles. A volume of 2 mL supernatant was used for determining of the Cu(II) concentrations. Dilution of samples was made with 0.01 M  $\text{H}_2\text{SO}_4$  solution.

Metal uptake ( $q_e$ ) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{1000W} \quad (8)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of total adsorbed Cu(II) ions,  $C_0$  ( $\text{mg L}^{-1}$ ) the initial metal concentration and  $C_e$  ( $\text{mg g}^{-1}$ ) the equilibrium metal concentration in solution at any time,  $V$  (L) the solution volume and  $W$  (g) the adsorbent weight.

The average percentage errors between the experimental and predicted values were calculated using Eq. (9).

$$\varepsilon (\%) = \frac{\sum_{i=1}^N |(q_e, i)_{\text{cal}} - (q_e, i)_{\text{exp}}| / (q_e, i)_{\text{exp}}}{N} \times 100 \quad (9)$$

where exp and cal show the experimental and calculated values of  $q_e$  and  $N$  is the number of measurements.

Control samples were prepared from the biomass free solution for testing metal losses due to metal precipitation and adsorption of flask surface. All experiments were carried out twice. Adsorbed metal concentrations were the means of the duplicate experimental results.

## 3. Results and discussion

### 3.1. General characterization of activated sludge and FT-IR analysis

Adana Organize Sanayi biological wastewater treatment system is nitrification–denitrification system and different industrial wastewaters have been treated in this system such as textile, paper, food, plastic, etc.

The total suspended solid, settable solid in 30 min and sludge age in wastewater treatment system are  $2.8 \text{ g L}^{-1}$ ,  $330 \text{ mL L}^{-1}$  and 14 day, respectively. Biosorbed divalent cations by activated sludge in activated sludge system were investigated and Pb(II), Ni(II), Cu(II) ions were not detected on dried activated sludge. The Cd(II), Zn(II) and Co(II) ions were determined as 0.08, 0.52 and  $0.06 \text{ mg g}^{-1}$ , respectively. The Ca(II) and Mg(II) were 0.135 and  $0.025 \text{ mg g}^{-1}$ , respectively.

The FT-IR analysis of dried activated sludge was given in Fig. 1. The band at  $3300 \text{ cm}^{-1}$  is O–H stretching of activated sludge polymeric compounds. A  $2927 \text{ cm}^{-1}$  asymmetric vibration of  $\text{CH}_2$ ,  $2852 \text{ cm}^{-1}$  symmetric vibration of

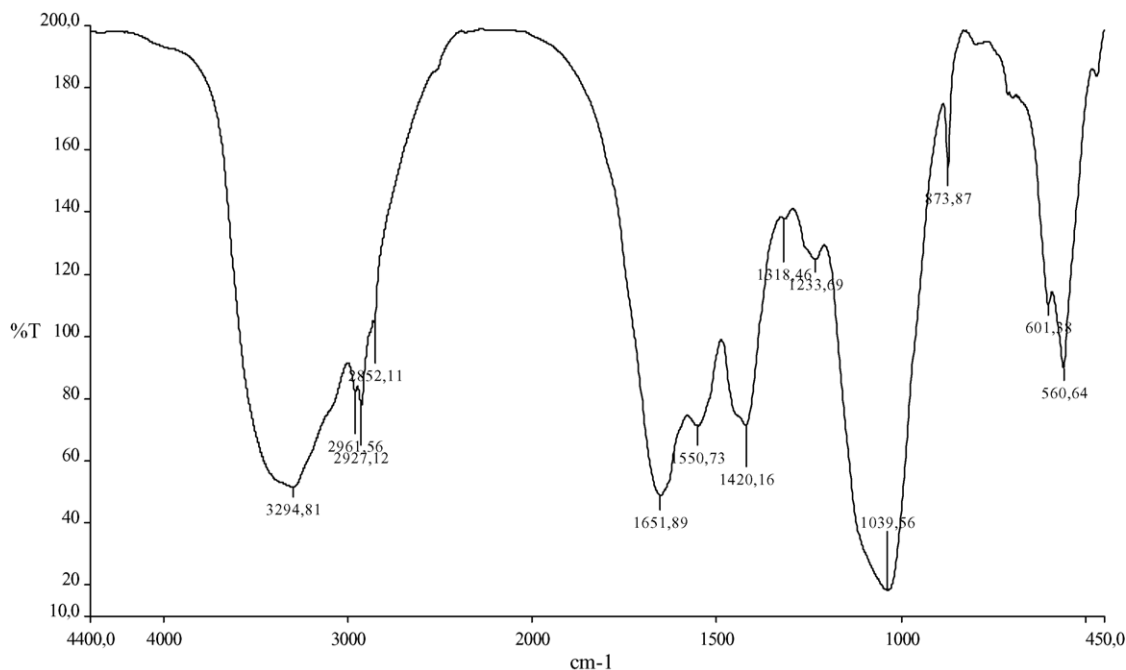


Fig. 1. FT-IR spectra of dried activated sludge.

$\text{CH}_2$ ,  $1651\text{ cm}^{-1}$  stretching vibration of  $\text{COO}$ ,  $\text{C}=\text{O}$  and  $\text{C}-\text{N}$  (amide I) peptidic bond of proteins. A  $1550\text{ cm}^{-1}$  band is stretching vibration of  $\text{C}-\text{N}$  of peptidic bond of proteins. A  $1420\text{ cm}^{-1}$  is of phenolic  $\text{O}-\text{H}$  and  $\text{C}=\text{O}$  stretching of carboxylates.  $1233\text{ cm}^{-1}$  band is vibration of carboxylic acids and stretching  $\text{OH}$  vibration phenolics. A  $1130\text{--}1000\text{ cm}^{-1}$  band is vibration of  $\text{C}-\text{O}-\text{C}$  and  $\text{OH}$  of polysaccharides. A  $873\text{ cm}^{-1}$  band  $\text{Si}-\text{H}$  bend. A  $<800\text{ cm}^{-1}$  is finger print zone which is phosphate and sulphur functional groups.

The microbial populations are organized as flocks in wastewater treatment system, which are composed of varying group organisms (bacteria, algae, fungus and protozoa, etc.), mineral particles and inorganic ions. The activated sludge is known as a rich organic mass. The biochemical composition of these organic mass are protein, lipid, extra cellular polysaccharides, nucleic acids, cell wall compositions and other cellular compounds of the microorganism. The characteristic bands of proteins, lipids, polymeric compounds and carboxylic acid groups were shown in FT-IR spectra of activated sludge. Results of FT-IR spectra show that dried activated sludge has different functional groups. These ionisable functional groups are able to react with protons or cations in aqueous solution [16].

### 3.2. Effect of pH and temperature on the biosorption capacity

Fig. 2 shows the effect of pH on biosorption of  $\text{Cu}(\text{II})$  onto dried activated sludge at  $20\text{ }^\circ\text{C}$ ,  $100\text{ mg L}^{-1}$  initial metal concentration,  $<0.063\text{ mm}$  particle size range and 60 min. The biosorption of  $\text{Cu}(\text{II})$  increases with increases in pH from 2.0 to 4.0. These results suggest that the biosorption of  $\text{Cu}(\text{II})$  on

biomass is mainly due to ionic attraction. At lower pH more protons will be available to protonate active groups of activated sludge biomass surface such as polysaccharides, lipids, amino acids and other cellular components of the microorganism. The metal ions are in competition with the  $\text{H}^+$  in the solution at low pH values for the biosorption on biomass surface active sites [26]. For biosorption studies pH value 4.0 was used. The optimal pH value of 4.0 was reported for biosorption of  $\text{Cu}(\text{II})$  by various marine algae [6]. The biosorption capacity of dried activated sludge at pH 4.0 was  $76\text{ mg L}^{-1}$ .

The effect of temperature on the biosorption were studied at  $20$ ,  $35$ ,  $50\text{ }^\circ\text{C}$  at  $100\text{ mg L}^{-1}$  initial metal concentration,  $<0.063\text{ mm}$  particle size range, pH 4.0 and 60 min. The results were given in Fig. 3. Biosorption capacities decreased with increasing temperature from  $20$  to  $50\text{ }^\circ\text{C}$ . Results indicated that biosorption of  $\text{Cu}(\text{II})$  was exothermic. The optimum temperature of biosorption was found to be  $20\text{ }^\circ\text{C}$  between the

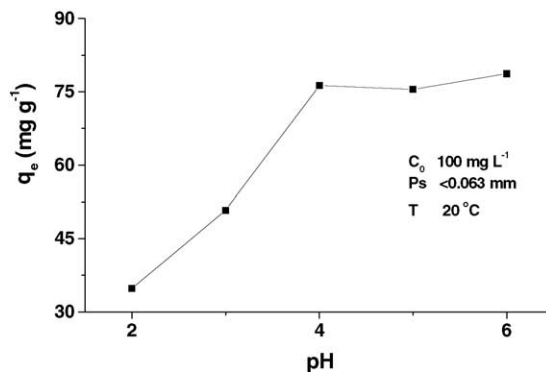


Fig. 2. Effect of pH on biosorption.

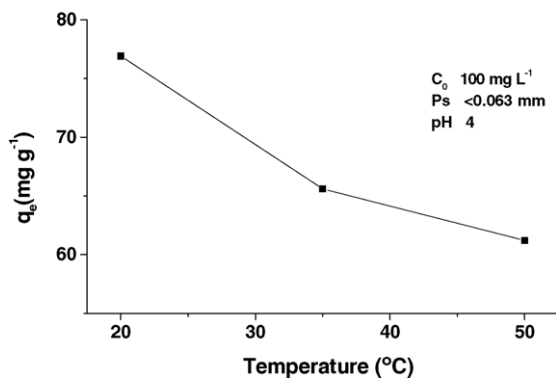


Fig. 3. Effect of temperature on biosorption.

studied temperatures ranges. Biosorption capacities of dried activated sludge were determined as 76, 67 and 60 mg g<sup>-1</sup> for 20, 35 and 50 °C, respectively.

### 3.3. Effect of initial metal concentration and particle size

Initial metal concentration provides important driving force to overcome all mass transfer resistances of the metal between the aqueous and solid phase [15]. The effect of initial metal concentrations was investigated between 100 and 400 mg L<sup>-1</sup> initial metal concentrations, at 20 °C and at pH 4.0. The results were given in Figs. 4–6. The biosorption capacity of dried activated sludge for <0.063 mm particle size range was determined as 76, 156 and 243 mg g<sup>-1</sup> for 100, 200 and 400 mg L<sup>-1</sup> initial metal concentrations, respectively. This indicated that initial Cu(II) concentration are important parameter for biosorption of Cu(II) by dried activated sludge biomass.

The contact surface of the biosorbent with metal ions in solution plays an important role for biosorption processes. The effect of particle size of dried activated sludge on Cu(II) removal was studied using three particle size groups, they were <0.063; 0.63–1.25; 1.25–2.50 mm. Effect of particle size on adsorption was given in Figs. 4–6. The capacity of Cu(II) biosorption at equilibrium increase with decrease of

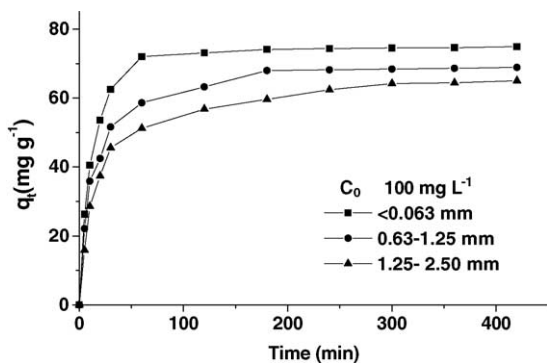


Fig. 4. Particle size effect on biosorption at pH 4 and 20 °C.

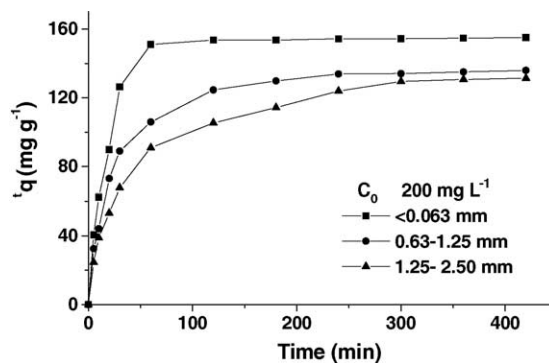


Fig. 5. Particle size effect on biosorption at pH 4 and 20 °C.

particle sizes. The biosorption capacity of activated sludge at 100 mg L<sup>-1</sup> initial metal concentrations were determined as 76, 70 and 66 mg g<sup>-1</sup> for <0.063; 0.63–1.25; 1.25–2.50 mm particle size, respectively. Similar results have been reported for adsorption of metal ions by natural polymers and Cd(II) by chitin [11,27]. The increasing of particle size of dried activated sludge was increased the equilibrium time. The equilibrium times were determined as 60, 180 and 300 min for <0.063; 0.63–1.25; 1.25–2.50 mm particle size, respectively.

### 3.4. Adsorption isotherm

The adsorption isotherms were studied at 20, 35 and 50 °C. A plot of linear Langmuir equation C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> is shown in Fig. 7. The value of isotherm constants, equilibrium monolayer capacities (q<sub>max</sub>) and standard deviation of linear regression were given in Table 1. Biosorption capacities of dried activated sludge decreased with increasing temperature. The equilibrium monolayer capacities, q<sub>max</sub>, were determined as 294, 286 and 276 mg g<sup>-1</sup> for Cu(II) 20, 35 and 50 °C, respectively. The plots in Fig. 7 show that the Langmuir equation provides an accurate description of the experimental data, which is further confirmed by the extremely high values of the correlation coefficients for Cu(II).

The R<sub>L</sub> values (Table 1) shows that biosorption behavior of dried activated sludge are favorable (0 < R<sub>L</sub> < 1). The low

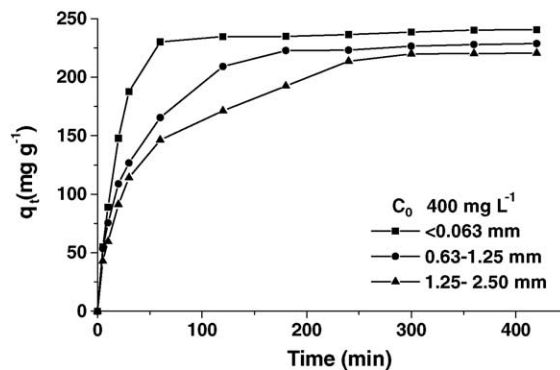


Fig. 6. Particle size effect on biosorption at pH 4 and 20 °C.

Table 1  
Langmuir and Freundlich isotherm constants

Temperature (°C)	Langmuir					Freundlich				
	$K_L$	$a_L$	$q_{max}$	$r^2$	$R_L$	S.D.	$K_F$	$n$	$r^2$	S.D.
20	5.26	0.018	294.0	0.996	0.0852	0.048	9.19	1.5	0.986	0.191
35	3.45	0.012	286.0	0.993	0.1213	0.076	6.05	1.4	0.989	0.145
50	2.22	0.008	276.0	0.986	0.1724	0.104	3.00	1.2	0.985	0.201

S.D.: standard deviation.

values of  $R_L$  indicated that biosorption tend to be weakly irreversible.

The Freundlich isotherm constants were given in Table 1, High correlation coefficient ( $r^2 > 0.985$ ) and the magnitude of exponent  $n$  indicated the favorability and the capacity of the adsorbent/adsorbate system.

The Langmuir model makes several assumptions, such as monolayer coverage and constant adsorption energy while Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. The applicability of both Langmuir and Freundlich isotherms to metal-activated sludge biomass implies that both monolayer adsorption and heterogeneous surfaces conditions exist under the experimental conditions used. The biosorption properties of the activated sludge are thus likely to be complex, involve more than one mechanism [28].

### 3.5. Pseudo first and second-order kinetic models

The effects of particle size and initial metal concentrations on biosorption kinetics were investigated. The biosorption kinetic constants, standard deviations of linear regression and the average percentage errors between the experimental and calculated data were given in Table 2.

If pseudo second-order kinetic models is applicable, the plot of  $t/q_t$  versus  $t$  should show a linear relationship. The pseudo second-order kinetic rate constant  $K_2$  and  $q_{e,cal}$  values were determined from the slope and intercept of the Fig. 8. The correlation coefficients for the pseudo second-order kinetic model obtained at all the studied concentrations were high ( $r^2 > 0.998$ ). Also the  $q_{e,cal}$  values fitted the experimental

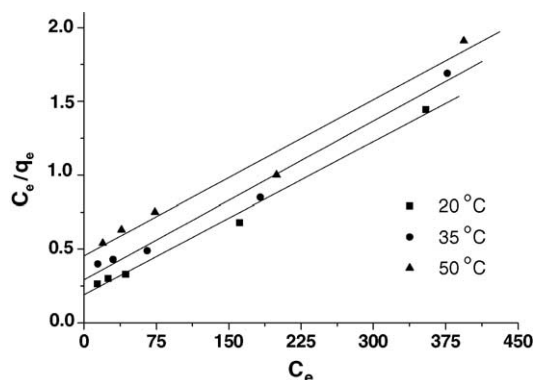


Fig. 7. Linear Langmuir adsorption isotherms at 25, 35 and 50 °C.

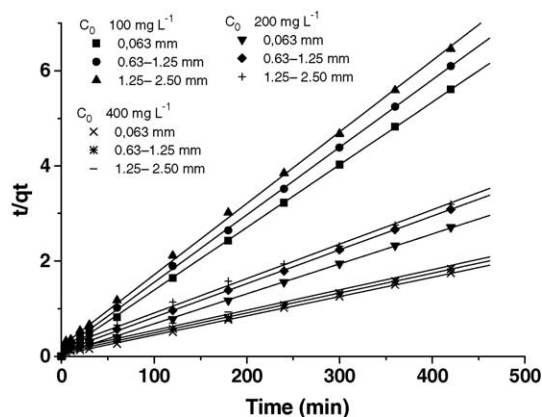


Fig. 8. Pseudo second-order adsorption kinetics at pH 4 and 20 °C.

data. These suggested that the pseudo second-order adsorption mechanism was predominant and that the overall rate of the Cu(II) adsorption process appeared to be controlled by chemical process [23].

The pseudo first-order kinetic rate constant  $K_1$  and  $q_{e,cal}$  values were determined from the slope and intercept of the Fig. 9. The correlation coefficients for the pseudo first-order kinetic constants obtained at all the studied concentrations and the correlation coefficients were low ( $r^2 < 0.970$ ). The calculated  $q_e$  values of first-order did not give reasonable values, which were too low to compare with experimental  $q_e$  values. The biosorption of Cu(II) onto dried activated sludge was not a pseudo first-order.

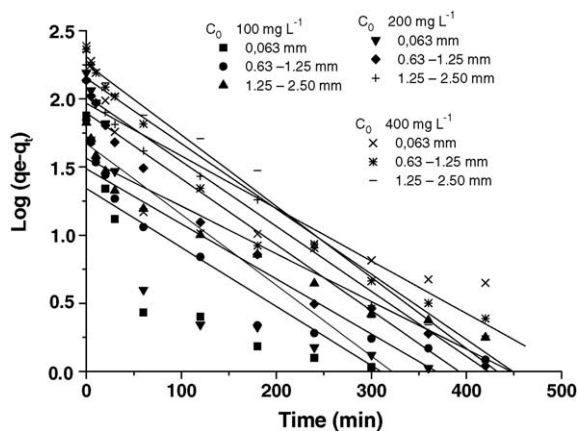


Fig. 9. Pseudo first-order adsorption kinetics at pH 4 and 20 °C.

Table 2  
Comparison of the pseudo first, second-order and intraparticle diffusion rate constants

$C_0$	100 mg L <sup>-1</sup>			200 mg L <sup>-1</sup>			400 mg L <sup>-1</sup>		
	$P_{s1}$	$P_{s2}$	$P_{s3}$	$P_{s1}$	$P_{s2}$	$P_{s3}$	$P_{s1}$	$P_{s2}$	$P_{s3}$
$q_{e \text{ exp}}$	76.00	70.00	66.00	156.00	137.00	122.00	243.00	231.00	222.00
Pseudo first-order kinetics									
$q_{e \text{ cal}}$	22.00	31.00	36.00	47.00	79.00	102.00	93.00	144.00	182.00
$\varepsilon$ (%)	35.50	28.17	22.38	34.90	21.01	8.23	30.79	18.72	9.06
$K_1 \times 10^{-3}$	9.97	9.30	8.06	11.97	11.10	10.90	8.98	11.03	12.02
$r^2$	0.875	0.934	0.937	0.871	0.945	0.964	0.877	0.952	0.967
S.D.	0.378	0.244	0.145	0.465	0.171	0.076	0.335	0.184	0.133
Pseudo second-order kinetics									
$q_{e \text{ cal}}$	76.00	70.00	67.00	159.00	141.00	138.00	247.00	239.00	235.00
$\varepsilon$ (%)	0.05	0.05	0.45	1.02	1.47	6.53	0.83	1.77	2.81
$h$	1.33	7.46	4.69	18.56	9.17	5.34	24.69	13.02	8.60
$K_2 \times 10^{-4}$	0.23	0.15	0.11	7.35	4.61	2.78	4.07	2.27	1.57
$r$	0.999	1.000	0.999	0.999	0.999	1.000	0.999	0.998	0.997
S.D.	0.036	0.054	0.088	0.033	0.040	0.076	0.021	0.031	0.050
Intraparticle diffusion									
$k_{i1}$	12.08	8.82	8.5	20.58	15.78	12.08	31.23	22.96	20.8
$k_{i2}$	0.57	1.631	1.42	0.15	3.57	4.14	0.555	7.76	7.943
$k_{i3}$	–	0.164	0.16	–	0.236	0.591	–	0.38	0.212
$q_{e \text{ cal}}$	77.9	73.6	68.6	162	139.2	133.9	249.5	237.7	224.9
$\varepsilon$ (%)	1.25	2.57	1.96	1.92	0.8	4.87	1.33	1.45	0.65
$r^2_1, r^2_2, r^2_3$	>0.992	>0.996	>0.993	>0.971	>0.997	>0.979	>0.976	>0.998	>0.998

Particle size ( $P_s$ ),  $P_{s1}$  (0.063 mm);  $P_{s2}$  (0.63–1.25 mm);  $P_{s3}$  (1.25–2.5 mm); S.D.: standard deviation.

### 3.6. The intraparticle diffusion model

The plot of  $q_t$  versus  $t^{0.5}$  may present multi linearity. The first shape portion is the external surface biosorption stage. The second shape is the gradual biosorption stage, where the intraparticle diffusion is rate-controlled. The third shape is the final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution [29–32]. Effects of particle size on intraparticle diffusion were given in Fig. 10. When the adsorption is reached saturation at exterior surface, the Cu(II) ions was entered pore within the dried activated sludge biomass for interaction of interior surface of dried activated sludge biomass [33]. The particle size of dried activated sludge of <0.063 mm

two shape were seen: the first shape portion was the external surface biosorption stage and the second shape was the final equilibrium stage. The adsorption occurs on to external surface of dried activated sludge biomass, due to the extremely low particle size.

The intraparticle diffusion rate constants ( $k_{i1}$ ,  $k_{i2}$  and  $k_{i3}$ ),  $q_{e \text{ exp}}$  and  $q_{e \text{ cal}}$  were given in Table 2. If intraparticle diffusion rate constants are compared, it is easy to see that  $k_{i1}$  (first stage) >  $k_{i2}$  (second stage) >  $k_{i3}$  (third stage). Similar results were reported for adsorption of basic dyes by modified peat-resin [29]. The diffusion rate was decreased with increasing the particle size.

## 4. Conclusion

In batch biosorption studies, data show that dried activated sludge has considerable potential for the removal of Cu(II) from aqueous solution. Optimum pH and temperature for biosorption in studied pH and temperature ranges were found as 4.0 and 20 °C, respectively. The maximum Cu(II) biosorption capacity of dried activated sludge was determined as 294 mg g<sup>-1</sup> at 20 °C and pH 4 for <0.063 mm particle size. Langmuir and Freundlich isotherms were fitted very well with studied temperature and concentration ranges. The biosorption capacity of dried activated sludge was decreased with increasing solution temperature; the biosorption of Cu(II) on dried activated sludge is exothermic reactions. The  $R_L$  values show that, dried activated sludge was favorable for the biosorption of Cu(II).

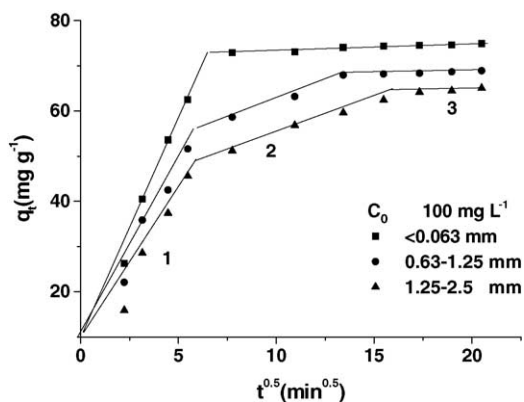


Fig. 10. Intraparticle diffusion kinetics at pH 4 and 20 °C.

The suitable kinetic models for the biosorption of Cu(II) onto dried activated sludge were also discussed. The pseudo-second kinetic model is applicable for describing of adsorption system. According to FT-IR results dried activated sludge has different functional groups. These functional groups are able to react with divalent cations in aqueous solution.

This study demonstrated that the activated sludge biomass could be used as an effective biosorbent for the treatment of wastewater containing Cu(II) ions. However activated sludge biomass is low cost natural abundant biomass and it may be alternative to more costly materials such as activated carbon.

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