Biosorption of copper (II) ions from synthetic aqueous solutions by drying bed activated sludge

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A B S T R A C T

In the present work, the usefulness of dried activated sludge has been investigated for the removal of copper ions from synthetic aqueous solutions. Kinetic data and equilibrium sorption isotherm were measured in batch conditions. The influence of some parameters such as: contact time, initial copper concentration, initial pH of solution and copper salt nature on copper biosorption kinetics has been studied. Copper uptake was time contact, initial copper concentration, initial pH solution and copper salt type dependent. Maximum copper sorption was found to occur at initial pH 5. Two simplified kinetic models including a first-order rate equation and a pseudo second-order rate equation were selected to describe the biosorption kinetics. The process followed a pseudo second-order rate kinetics. The process mechanism was found to be complex, consisting of external mass transfer and intraparticle mass transfer diffusion. Copper biosorption process was particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages for the different experimental parameters studied. Langmuir and Freundlich models were used to describe sorption equilibrium data at natural pH of solution. Results indicated that the Langmuir model gave a better fit to the experimental data than the Freundlich model. Maximum copper uptake obtained was $q_m = 62.50$ mg/g (0.556 mmol/g) under the investigated experimental conditions. Scanning electron microscopy coupled with X-ray energy dispersed analysis for copper-equilibrated dried activated sludge demonstrated that copper existed on its surface.

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1. Introduction

The presence of heavy metals in the aquatic environment is a source of great environmental concern. Copper is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment [1,2]. The potential sources of copper in industrial effluents include metal cleaning and plating baths, electrical industry, chemical catalysis, pulp, paper board mills, wood pulp production, the fertilizer industry, etc. The conventional methods of copper (II) removal from wastewaters are precipitation, ion exchange, electrolysis, adsorption on activated carbon, etc. [2,3]. They become inefficient and expensive especially when the heavy metal concentration is less than 100 ppm [4–6]. This situation has in recent years led to a growing interest in the application of biomaterials technology for removal of trace amounts of toxic metals from dilute aqueous wastes. Biomaterials including algae, bacteria, fungi, higher plants, and products derived from these organisms, have been demonstrated to remove certain chemicals species [7–9]. Stabilized activated sludge from drying bed is a by-product from

wastewater treatment plants, and contains significant amounts of heavy metals, organic toxins and pathogenic microorganisms, which are considered to be harmful to the environment and all living organisms. Agricultural use, land filling and incineration are commonly used as disposal methods [10]. Dried activated sludge may also be used as a low cost abundant material for the removal of heavy metal ions: it may be an alternative to more costly materials such as activated carbon. The general term "biosorption" has been used to describe a property of microorganisms to retain toxic heavy metals from aqueous solutions [11]. In spite many types of activated sludge have been demonstrated to remove heavy metals ions from aqueous solutions in the literature [12–22], their suitability, the mechanism involved and the factors governing the sorption are still not fully understood clearly. Also, it should be noted that the results reported in the literature on this subject have been performed in different testing conditions (e.g., pH, temperature, etc.), type of biosorbent material (sewage/aerobic/anaerobic activated sludge, dead or lived, age, nature of effluent, etc.) and method.

In this work, biosorption of copper (II) ions from synthetic aqueous solutions by dried activated sludge, in single metal solutions, was investigated in batch conditions. Kinetic experiments were performed at various contact time, initial copper concentration, initial pH and copper salt nature. Two simplified kinetic models, namely, a first-order rate model and a pseudo-second

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Nomenclature

B	constant of Boyd's model (min^{-1})
C_0	initial metal ion concentration (mg/L)
C_t	time metal ion concentration (mg/L)
C_e	equilibrium metal ion concentration (mg/L)
F	fraction of solute sorbed
K_L	Langmuir model constant
K_F	Freundlich model constant
k_L	Lagergren rate constant of sorption (min^{-1})
k	pseudo second-order rate constant of sorption ($g\,mg^{-1}\,min^{-1}$)
k_i	intraparticle diffusion rate parameter ($mg\,metal/g\,sorbent\,time^{-0.5}$)
m	dried activated sludge weight in dry form (g)
n	Freundlich model constant
q_t	amount of metal ion sorbed at time t (mg/g)
q_e	amount of metal ion sorbed at equilibrium (mg/g)
q_m	maximum metal ion sorption capacity (mg/g)
R^2	regression coefficient
S	specific surface area (m^2/g)
t	time (min)
V	volume of solution (mL)
β_L	external mass transfer coefficient
$\beta_L S$	external mass transfer rate

order rate model, were selected to analyse the kinetic data obtained. To identify the main rate controlling steps in the overall uptake mechanism, a single external mass transfer diffusion model and intra-particle mass transfer diffusion model were used. The biosorption equilibrium data were obtained at natural pH of solutions and described by Langmuir and Freundlich sorption models. Spectroscopic techniques SEM/EDAX were used to characterize this material used, before and after equilibration with the copper ion, in an attempt to better understand the mechanism of the removal. These fundamental data will be useful for further applications in the treatment of practical waste or process effluents and may contribute to a better understanding or application of the biosorption phenomena at the liquid/solid interface.

2. Materials and methods

2.1. Biosorbent material and metal ion

Dried activated sludge was collected in February 2001, from drying bed of a conventional biological wastewater treatment plant in Maghnia, Algeria, in a solid form. After grinding and sieving in the form having a 0.2–5.0 mm particle size, it was ambient dried in the laboratory during one month. Further, it was used throughout this work without any preliminary purification. Prior to biosorption experiments, as a preliminary step for the subsequent evaluation of metal uptake capacity, its original content in heavy metal ions namely: copper and cadmium due to the ready availability of their ion selective electrodes in our laboratory, was evaluated using different acids HCl, HNO$_3$, and H$_2$SO$_4$ (0.01 N), respectively, and distilled water. From the results obtained at equilibrium after 24 h of contact solution-activated sludge under the experimental conditions used here (2 g/L, 400 rpm and 25 °C), it was concluded that this dried activated sludge contained little/negligible copper ions initially [23]: 18 mg/g with H$_2$SO$_4$ (0.01 N) and traces with distilled water. In the same time under these conditions, great amounts of cadmium ions were also leached from the biosorbent: about 15, 54, 104, 0.004 mg/g with HCl, HNO$_3$, H$_2$SO$_4$ (0.01 N) and distilled water respectively.

Spectroscopic techniques SEM/EDAX using a scanning electron microscope (JOEL JSM-64 000) were used to characterize this material used, before and after equilibration with the copper ions.

Copper solutions of desired concentration were prepared from Cu (NO$_3$)$_2$·4H$_2$O (Fluka), by dissolving the exact quantities of copper salts in distilled water. All chemicals were commercial products used without purification.

2.2. Biosorption kinetics

The initial solution metal concentration was 100 mg/L for all experiments except for that carried out to examine the effect of the initial concentration of copper. For metal removal kinetics studies, 0.6 g of dried activated sludge was contacted with 0.3 L of metal solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25 °C. In all cases, the working pH was that of the solution and was not controlled. The residual copper concentration in the aqueous solution at appropriate time intervals, was obtained by using a Cu^{2+}-ion selective electrode technique. Based on the ready availability of this electrode in our laboratory, this method was chosen. The electrode used for measurement of copper was Orion Model 9429 and was used in conjunction with Orion Model 06 237.100 reference electrode and an Orion Model 710A meter. For the measurement of pH, an Orion Model 9107 combination electrode with the aforementioned meter was used. For certain experiments, this copper concentration was also obtained using a Perkin Elmer Model 2280 atomic absorption spectrophotometer. No differences in the results obtained by these two methods of analysis were observed. The metal uptake q_t (mg ion metal/g dried activated sludge) was determined as follows:

$$q_t = (C_0 - C_t) \times \frac{V}{m} \tag{1}$$

where C_0 and C_t are the initial and time metal ion concentrations (mg/L), respectively, V is the volume of solution (mL), and m is the dried activated sludge weight (g).

To study the influence of pH of copper solution, the initial pH value was varied within the range 3–6 to ovoid metal solid hydroxide precipitation. Initial pH was adjusted to the required value by adding small amounts of 0.1 N HNO$_3$/NaOH.

Blank runs with only the biosorbent in 100 mL of distilled water, were conducted simultaneously at similar conditions to understand the pH change of solution during biosorption experiments. Blanks were also run without the biosorbent to determine the impact of pH change on the metal solution. Preliminary experiments had shown that copper sorption losses to the container walls were negligible.

2.3. Biosorption isotherm

The equilibrium isotherm was determined by contacting a constant mass 0.2 g of dried activated sludge with a range of different concentrations of copper solutions: 10–1100 mg/L. Mixtures sludge-solution were agitated in a series of 250 mL conical flasks with equal volumes of solution 100 mL for a period of 24 h at room temperature 25 ± 1 °C. This contact time was beyond to that previously determined by kinetics tests using the same conditions to ensure that equilibrium was reached. The mixture pH was not controlled after the initiation of experiments. After shaking the flasks, the equilibrium pH was measured. The concentration of unbound copper ions at equilibrium was obtained using a Cu^{2+}-ion-selective electrode (Cu-ISE) technique and the copper loading by activated sludge was determined.
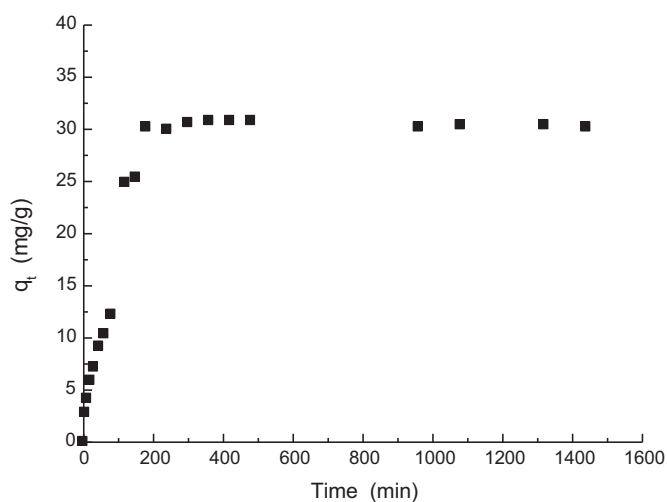
All studies were carried out in duplicate.

Fig. 1. Kinetics of copper biosorption by dried activated sludge (initial copper concentration = 100 mg/L, sorbent dose = 2 g/L, natural solution initial pH, agitation speed = 400 rpm, and T = 25 °C).

Fig. 2. Effect of initial pH on the kinetics of copper biosorption by dried activated sludge (initial copper concentration = 100 mg/L, sorbent dose = 2 g/L, agitation speed = 400 rpm, and T = 25 °C).

3. Results and discussion

3.1. Biosorption kinetics

3.1.1. Effect of contact time

A preliminary experiment was performed to determine the equilibrium time. According to Fig. 1 obtained for an initial copper concentration 100 mg/L, the kinetics of copper biosorption by dried activated sludge presents a shape characterized by a strong increase of the amount of copper biosorbed during the first minutes of contact solution-activated sludge, follow-up of a slow increase until to reach a state of equilibrium. The necessary time to reach this equilibrium is about 5 h and an increase of removal time to 24 h does not show notable effects. At equilibrium, about 56% of initial copper solution was removed by dried activated sludge (q_e = 30.36 mg/g) under these experimental conditions.

During the course of copper biosorption by dried activated sludge, a slight decrease in the initial pH value ($\triangle$pH = pH$_0$ − pH$_e$ = 0.15 unit) of the solution between the initial and equilibrium time was observed. In order to investigate the reason of this initial pH value change, experiments were performed with the biosorbent material tested in distilled water under the same conditions in absence of copper ions. Initial pH value of solution (figure not shown here) exhibited an increase ($\triangle$pH = pH$_e$ − pH$_0$ = 1.58 unit) that can be interpreted as a possible fixation of H$_3$O$^+$ ions by the negative groups present on the biosorbent surface.

Concerning the decrease in its value in the presence of copper ions, it can be interpreted as a possible release of H$_3$O$^+$ ions into the solution due to copper ions biosorption. The same tendencies were observed with other systems sorbent–metal [24–27]. An opposite trend was observed during the sorption of copper ions by sunflower leaves [28] and fig leaves [24] and for other systems metal–sorbent [29–35]. At this stage, further investigations are required to understand the mechanisms involved in copper biosorption by this type of complex natural materials.

3.1.2. Effect of initial copper concentration

Several experiments were also undertaken to study the effect of the initial copper concentration (20–500 mg/L), on the copper biosorption kinetics from solution by dried activated sludge. Initial metal concentration provides an important driving force to overcome 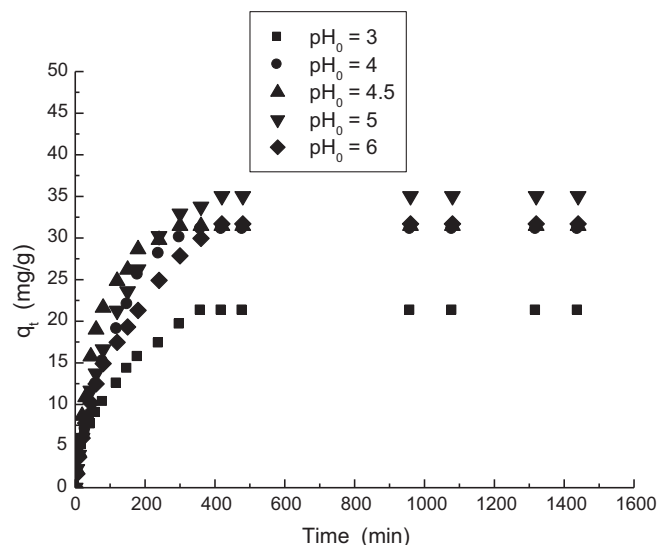all mass transfer resistances of the metal ion between the aqueous and solid phases. Hence a higher initial concentration of copper will enhance the biosorption process [36]. For all concentrations studied, the obtained curves have the same shape (figure not shown here). From the results obtained at equilibrium, the necessary time to reach equilibrium was in the range of 2.5–7 h with no clear tendency about its evolution with the initial metal concentration. The amount of copper biosorbed at the equilibrium increases with the initial copper concentration: 9.21 mg/g (C_0 = 20 mg/L) and 59.41 mg/g (C_0 = 500 mg/L).

3.1.3. Effect of initial pH

The pH of metal bearing wastewater varies greatly. The interaction between sorbate and sorbent is affected by the pH of an aqueous medium in two ways: firstly, since metal ions can have different speciation forms at different pH. Secondly, the surface of the biosorbent consists of biopolymers with many functional groups, so the net charge on biosorbent, is also pH dependent [37]. Thus, the effect of pH in the solution on the removal efficiency of Cu (II) by dried activated sludge was studied at different pH values in the range 3–6. The distribution diagrams of copper species as a function of pH show that only cationic species (Cu^{2+}, Cu(OH)$^+$) are present in solution over this range studied [38]. As shown in Fig. 2, the initial pH of copper solution has an influence on the kinetics of copper biosorption by dried activated sludge. The necessary time to reach equilibrium was in the range of 6–7 h depending on initial pH of solution. The amount of copper biosorbed at the equilibrium increases with the initial pH value: 21.25 mg/g (pH$_0$ = 3) and 35.03 mg/g (pH$_0$ = 5) and decreases beyond this last value of pH$_0$ to 31.70 mg/g (pH$_0$ = 6). These observations can be explained by the fact that at lower pH values, the surface charge of the biosorbent is positive, which is not favourable to copper ion biosorption. Meanwhile, hydrogen ions compete strongly with metal ions for the active sites, resulting in less biosorption. With increasing pH from 3 to 5, electrostatic repulsions between copper ions and surface sites and the competing effect of hydrogen ions decrease: consequently, the metal biosorption increases. Other authors [38] have found the same trend for copper sorption by other sorbent materials. Beyond pH 5, insoluble copper hydroxide starts precipitating resulting in lower amount of copper biosorbed at equilibrium.
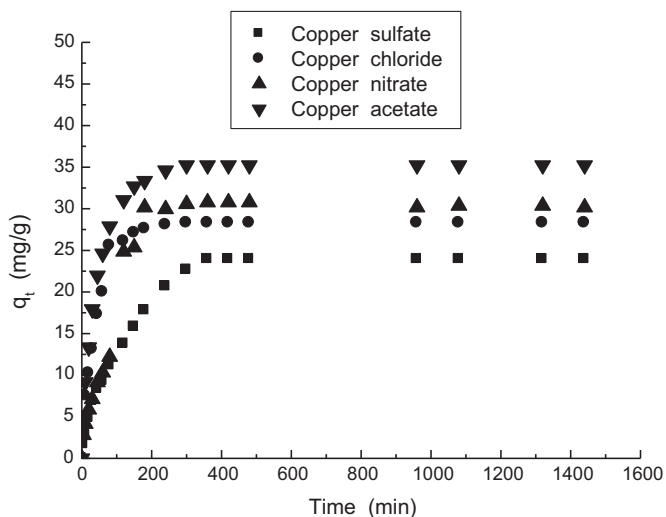
Fig. 3. Effect of copper salt nature on the kinetics of copper biosorption by dried activated sludge (initial copper concentration = 100 mg/L, sorbent dose = 2 g/L, natural solution initial pH, agitation speed = 400 rpm, and T = 25 °C).

3.1.4. Effect of copper salt nature

Fig. 3 shows that the nature of copper salt used influences the amount of copper biosorbed at equilibrium and the time required to reach equilibrium.

The amount of copper biosorbed by dried activated sludge at equilibrium is variable and salt nature depending: 30.77 mg/g (copper nitrate), 35.22 mg/g (copper acetate), 28.31 mg/g (copper chloride), and 23.94 mg/g (copper sulphate). The necessary time to reach equilibrium was dependent on the nature of copper salt used: 5 h (copper nitrate and copper acetate), 4 h (copper chloride), and 6 h (copper sulphate).

During the phenomenon of copper biosorption, in general, a decrease in the initial pH value of solutions (figure not shown here) was also observed [23]. Concerning the effect of initial solution pH, except for pH_0 = 6, an opposite tendency to that mentioned above, i.e. an increase in its value was observed for all the other values of initial pH.

3.1.5. Modelling

To analyse the kinetic data of copper biosorption by dried activated sludge under the different experimental conditions tested, two common equations from the literature, namely, the first-order rate model of Lagergren [39] and the pseudo second-order rate model [40] were chosen and shown below as Eqs. (2) and (3) in their linear forms:

$$\log(q_e - q_t) = \log q_e - \frac{k_L t}{2.3} \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k.q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_L is the Lagergren rate constant of sorption (min^{-1}) and k is the pseudo second-order rate constant of sorption ($g\,mg^{-1}\,min^{-1}$); q_e and q_t are the amounts of copper biosorbed (mg/g) at equilibrium and at time t, respectively. For all initial copper concentrations, the different values of constants from the slope and intercept of linear plots of $\log(q_e - q_t)$ vs. t and t/q_t vs. t (figures not shown here) are summarized in Table 1.

Compared to the first-order rate equation (R^2 = 0.9336–0.9964), the pseudo second-order rate model adequately described the kinetics of copper biosorption with acceptable correlation coefficient (R^2 = 0.9925–0.9997). The equilibrium copper biosorption capacity, q_e, increases with the increase in the initial copper concentration. The values of q_e obtained from the fitting to the pseudo

second-order rate model are very similar to the experimental values obtained from the biosorption kinetics at equilibrium: consequently, it was further used to describe all the kinetics of copper biosorption by dried activated sludge obtained under other experimental conditions. The results obtained and also presented in Table 1 confirm that the kinetic data obtained follow the pseudo second-order kinetic model. In this model, all the steps of sorption such as: external diffusion, internal diffusion, and sorption are lumped together and it is assumed that the difference between the average solid phase concentration and the equilibrium concentration is the driving force for sorption, and that the overall sorption rate is proportional to the square of the driving force [41].

3.1.6. Rate determining steps

From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during the sorption process. It is generally agreed that there are four consecutive steps which describe the overall sorption process of solute from a solution by a sorbent particle [42]. These steps, as adapted to apply to the sorption of metal ions by a sorbent particle, are as follows:

1. External mass transfer of the metal ions from the solution bulk to the boundary film.
2. Metal ions transport from the boundary film to the surface of the sorbent particle.
3. Diffusion of the metal ions within the sorbent particle to the sorption sites: internal diffusion of metal ions.
4. Final uptake of metal ions at the sorption sites, via complexation, sorption, or precipitation, which is fast.

The first and the second step are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. In this study, the agitation given here to the solution (400 rpm) is considered as sufficient to avoid steps 1 and 2 being controlling steps [23]. In a well-agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient; hence, the third intraparticle diffusion resistance step is more likely to be the rate controlling step [43]. In the process of establishing the rate limiting step, the fourth step is assumed to be very rapid and is therefore not considered in any kinetic analysis [44]: sorption is a quasi-instantaneous process, as well as complexation mechanism, precipitation seems to occur with a lower rate [11]. The sorption rate will be controlled by the rate of diffusion [45]. Consequently, the two rate limiting steps investigated are external film mass transfer and intraparticle diffusion, either singly or in combination. Models were established to determine the two coefficients initially based on single resistance mass transport analysis [46].

3.1.6.1. External mass transfer resistance model.
This model assumes that the surface solute concentration, C_s, on the sorbent is negligible at t = 0, and that intraparticle diffusion is also negligible; it is applied to calculate the initial rate of solute sorption [47]. The initial rate of sorption can be determined using the classic mass transfer equation (4) which describes the evolution of solute concentration C_t in solution:

$$\frac{dC_t}{dt} = -\beta_L S(C_t - C_s) \tag{4}$$

where β_L is the external mass transfer coefficient, C_t is the liquid phase solute concentration at a time t, C_s is the liquid phase solute concentration at the particle surface and S is the specific surface area for mass transfer.

Table 1
Model rate constants for copper biosorption kinetics by dried activated sludge.

	q_e exp. (mg/g)	First-order kinetics model				Pseudo second-order kinetics model		
		q_e cal. (mg/g)	k_L ($\times 10^3$ min^{-1})	R^2		q_e cal. (mg/g)	k' ($\times 10^4$ g mg^{-1} min^{-1})	R^2
C_0 (mg/L)					Initial copper concentration			
20	9.21	8.06	18.45	0.9790		9.36	63.60	0.9997
60	23.02	21.76	8.54	0.9912		24.36	6.60	0.9971
100	30.77	39.90	17.20	0.9336		32.18	5.10	0.9925
200	49.08	41.68	70.94	0.9911		51.36	3.80	0.9982
300	52.92	44.60	12.83	0.9964		54.29	6.90	0.9995
400	54.79	56.49	18.70	0.9942		56.43	6.20	0.9981
500	59.41	57.55	17.34	0.9919		60.72	7.50	0.9995
pH$_0$					Solution initial pH			
3	21.25					22.55	6.70	0.9973
4	31.04					32.43	6.80	0.9978
4.5	31.45					32.70	7.62	0.9985
5	35.03					37.69	3.30	0.9968
6	31.70					34.34	3.20	0.9970
Salt					Copper salt nature			
Nitrate	30.77					32.18	5.10	0.9925
Acetate	35.22					35.95	13.50	0.9996
Chloride	28.31					28.86	18.10	0.9994
Sulphate	23.94					25.63	5.20	0.9968

This equation can be simplified, by substituting the following boundary conditions: $C_t \to C_0$ and $C_s \to 0$ when $t \to 0$; C_0 = initial solute concentration [38–40], to:

$$\frac{d(C_t/C_0)}{dt} = -\beta_L S \tag{5}$$

So the external mass transfer rate, $\beta_L S$, is approximated by the initial slope of the C_t/C_0 vs. time graph and can be calculated either by assuming a polynomial relation between C_t/C_0 and time or based on the assumption that the relation-ship was linear for the first initial rapid phase. The first technique was used here.

3.1.6.2. Intraparticle diffusion resistance model. Weber and Morris [48] demonstrated that in intraparticle diffusion studies, rate processes are usually expressed in terms of square root of time. So q_t or fraction solute sorbed is plotted against $t^{0.5}$ as follows:

$$q_t = k_i t^{0.5} + C \tag{6}$$

where q_t is the solute concentration in the solid, k_i is the slope of the plot defined as an intraparticle diffusion rate parameter and C is proportional to the boundary layer thickness.

Initial slope is determined by the derivative (at $t = 0$) of the polynomial linearisation of q_t vs. $t^{0.5}$. If particle diffusion is rate controlling, the plots q_t vs. $t^{0.5}$ are linear and the slope of the plots is defined as an intraparticle diffusion rate parameter, k_i (mg metal/g sorbent time$^{-0.5}$) [46]. In theory, the plot between q_t and $t^{0.5}$ is given by four regions representing the external mass transfer followed by intraparticle diffusion in macro, meso and micropore [49].

Fig. 4a and b (as a typical example) shows plots of C_t/C_0 vs. time and q_t vs. $t^{0.5}$ for the effect of initial copper concentration on copper biosorption kinetics by solid activated sludge. Table 2 summarizes the mass transfer coefficients for the different kinds of transfer resistance.

As shown in Table 2, the values of mass transfer coefficients obtained are different and dependent on the experimental parameter studies. In Fig. 4b showing q_t vs. $t^{0.5}$, three linear portions were observed in the same experiment: a first linear portion followed by two other linear portions before equilibrium indicating multiple-stage diffusion of copper onto dried activated sludge particles. Such a multiple nature of the curve confirms that intraparticle diffusion is not a fully operative mechanism for this system and reflects two stages: external mass transfer at initial time periods followed by intraparticle diffusion of copper onto activated sludge particles. The

Table 2
Effect of different experimental parameters on diffusion coefficients for copper biosorption by dried activated sludge.

Parameter	External mass transfer model	Intraparticle diffusion model	
	$\beta_L S$ (10^3 min^{-1})	k_i (mg/g min$^{-0.5}$)	C (mg/g)
C_0 (mg/L)		Initial copper concentration	
20	31.82	0.08	7.74
60	12.58	0.50	12.53
100	11.46	0.11	28.68
200	11.47	2.06	9.73
300	8.75	0.60	41.58
400	4.11	3.32	13.32
500	7.25	1.25	40.11
pH$_0$		Solution initial pH	
3	6.98	1.02	1.78
4	5.84	0.85	15.09
4.5	8.66	0.72	18.93
5	6.04	0.66	21.49
6	6.74	1.21	6.85
Salt		Copper salt nature	
Nitrate	10.11	0.11	28.68
Acetate	18.35	0.51	26.48
Chloride	12.50	0.23	24.40
Sulphate	5.87	0.94	6.11

slope of the third linear portion characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept, C (mg/g), is proportional to the boundary layer thickness: the larger intercept the greater is the boundary layer effect [50]. For all experimental parameters studied, except some cases, positive and significant ordinate intercepts, C (mg/g), is obtained indicating the influence of external rate control [45].

These observations indicate that copper biosorption by dried activated sludge is a complex process. Thus, in order to determine the actual rate-controlling step involved in copper biosorption process, the biosorption data were further analysed by the kinetic expression given by Boyd et al. [51]:

$$F = 1 - \left(\frac{6}{\pi^2}\right) \exp(-Bt) \tag{7}$$

where F is the fraction of solute sorbed at different times t and Bt is a mathematical function of F and given by:

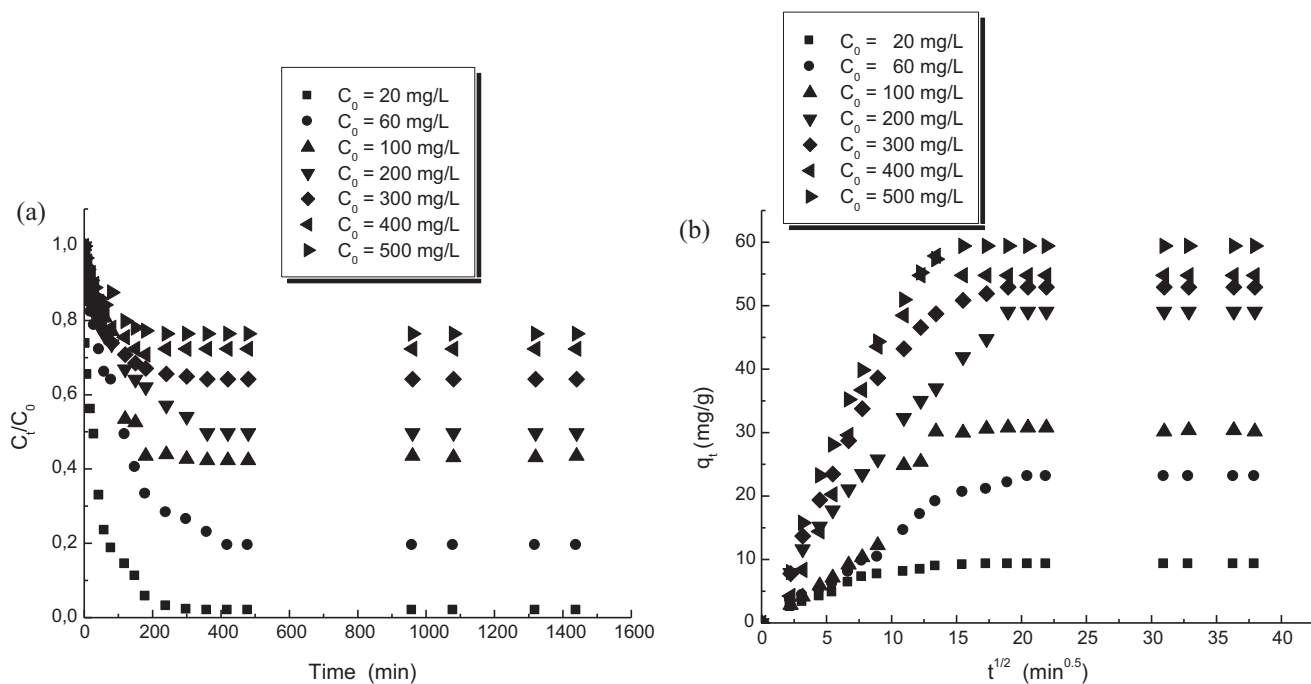$$F = \frac{q_t}{q_\infty} \tag{8}$$

Fig. 4. Diffusion plots for copper biosorption kinetics by dried activated sludge: effect of initial copper concentration (as a typical example): (a) C_t/C_0 vs. t and (b) q_t vs. $t^{0.5}$.

where q_t and q_∞ represent the amount of solute sorbed (mg/g) at any time t and at infinite time.

Substituting Eq. (7) into Eq. (8), the kinetic expression becomes:

$$Bt = -0.4967 - \ln\left(1 - \frac{q_t}{q_\infty}\right) \qquad (9)$$

Thus, the value of Bt can be calculated for each value of F using Eq. (9). These values were plotted against time. The linearity of this plot will provide useful information to distinguish between external transport and intraparticle transport controlled rates of sorption [50]. For all experimental parameters studied, it was observed (see Fig. 5, as a typical example) that the plots were linear but did not pass through the origin, indicating that external mass transport mainly governs the rate-limiting process [51].

3.2. Biosorption equilibrium

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions [52,53]. Fig. 6 shows the copper biosorption isotherm (q_e vs. C_e) by dried activated sludge at natural pH of solutions which is of L type according to the classification of Giles et al. [54] for liquid–solid adsorption. From the plot of this isotherm, the maximum capacity of copper biosorbed by activated sludge is about 60 mg/g under these experimental conditions.

During the experiments of copper biosorption equilibrium, it was also observed that the initial pH value of solutions slightly decreased and the pH value at equilibrium varied with the initial copper concentration [23].
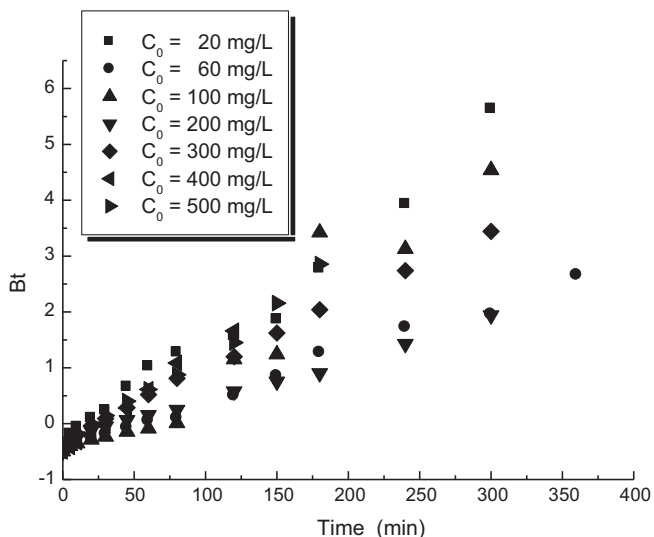

Fig. 5. Boyd's model plot for copper biosorption kinetics by dried activated sludge: effect of initial copper concentration (as a typical example).
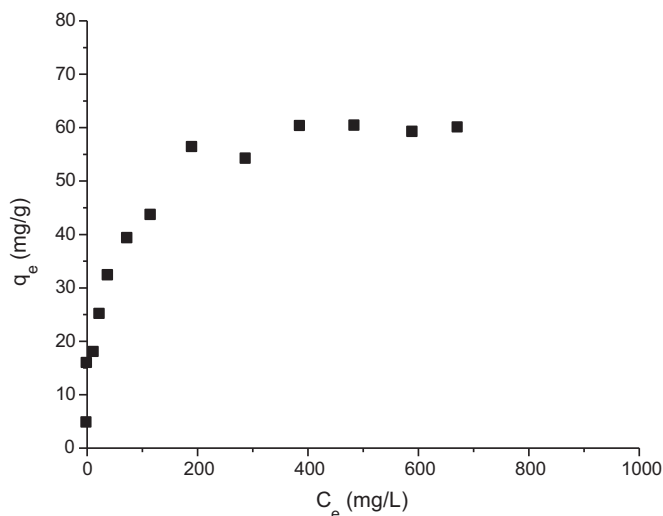

Fig. 6. Isotherm of copper biosorption by dried activated sludge at 25 °C (sorbent dose = 2 g/L, initial pH no adjusted, and agitation speed = 400 rpm).

In order to optimise the design of a sorption system to remove pollutant from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested in the present study, namely, Langmuir [55] and Freundlich [56]. This modelling permits us to determine the maximal capacity of biosorption.

The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an R^2 value closest to unity is deemed to provide the best fit.

(a) The Langmuir model has the following form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (10)$$

with q_e is the amount of metal ion sorbed at equilibrium per g of sorbent (mg/g), q_m is the maximal metal sorption capacity of sorbent material (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L) and K_L is the constant of equilibrium (L/mg) depending on temperature and the applied conditions. This equation can be linearised under the following shape:

$$\frac{C_e}{q_e} = \frac{1}{K_L . q_m} + \frac{C_e}{q_m} \qquad (11)$$

If the equation of Langmuir is valid to describe the experimental results, it must verify the linearised shape of the basis equation, in system of coordinates $C_e/q_e = f(C_e)$, that will permit to obtain the constants q_m and K_L from the intercepts and slopes.

(b) The Freundlich model has the form:

$$q_e = K_F C_e^n \qquad (12)$$

where q_e and C_e are as described before, K_F and n are the positive constants depending on the nature of system solute–sorbent and temperature, $n < 1$. This equation can be linearised under the following form:

$$\mathrm{Ln}\, q_e = \mathrm{Ln}\, K_F + n\, \mathrm{Ln}\, C_e \qquad (13)$$

If this equation is verified with data of sorption equilibrium, we must obtain a straight line in the system of coordinates $\mathrm{Ln}\, q_e = f(\mathrm{Ln}\, C_e)$, the slope and the intercept to the origin give the values of constants n and K_F respectively.

From results obtained (figures not shown here), it appears that the Langmuir model acceptably fits the experimental results over the experimental range with good coefficients of regression. The model parameters determined by least squares fit of the experimental sorption data are: $q_m = 62.50$ mg/g (0.556 mmol/g),

$K_L = 0.037$ L/mg ($R^2 = 0.996$). According to coefficients of correlation $R^2 = 0.900$ obtained with $K_F = 12.62$ and $n = 0.25$, the model of Freundlich is not adequate for modelling the isotherm of copper biosorption by dried activated sludge in all the studied concentration domain. The applicability of these models should be considered as a mathematical representation of the sorption equilibrium over a given metal ion concentration range. The mechanistic conclusions from the good fit of the models alone should be avoided.

In spite of these limitations, these models can provide information on metal-uptake capacities for any performance comparison between various sorbent materials [57]. According to Artola et al. [22], the sorption of metal by the sludge is a consequence of the interaction between metal ions in the aqueous phase and the cell wall of bacteria. The activated sludge biomass is known as a rich organic mass and composes of microorganisms (bacteria, algae and protozoa) and inorganics. The biochemical composition of this organic mass are protein, lipid, extra cellular polysaccharides, nucleic acids, cell wall compositions and other cellular compounds of the microorganism which are able to interact with metal ions in aqueous solutions [36]. For comparison, this copper biosorption capacity obtained by the dried activated sludge is also higher than those of some other sorbent materials reported in the literature (see Table 3) although this direct comparison is difficult due to the varying experimental conditions used in these studies. Differences of metal uptake are due to the properties of each sorbent material such as structure, functional groups and surface area [2].

Table 3
Comparison of maximum capacities of some sorbents materials for copper (II) ions sorption, from the literature.

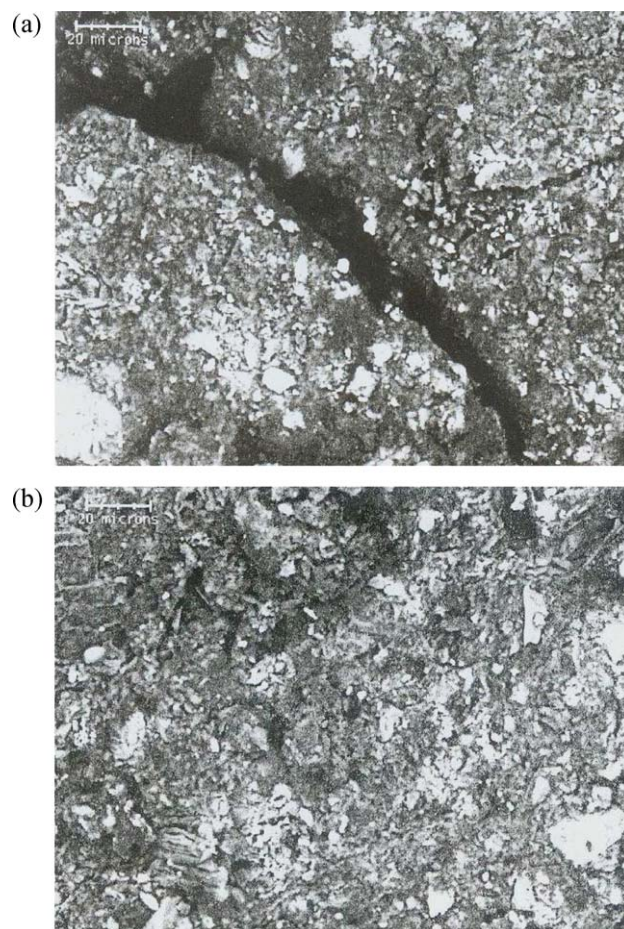| Sorbent material	q_m (mg/g)	Reference
P. chrysosporium	248.15	[58]
Bacillus subtilis	146.09	[59]
Dried sunflower leaves	89.37	[28]
Penicillium ochrochloron	80.70	[60]
Peanut hull carbon	65.57	[61]
Dowex 50X8-200	66.08	[58]
Dried activated sludge	62.50	This work
Chitin	29.04	[62]
Kaolinite	10.79	[63]
Activated sludge	7.94	[64]
Cellulose	7.06	[65]
Lignite	6.35	[66]
Perlite	0.26	[67]

Fig. 7. SEM micrographs of dried activated sludge (500×): (a) in the absence of copper and (b) after copper biosorption ($C_0 = 100$ ppm).
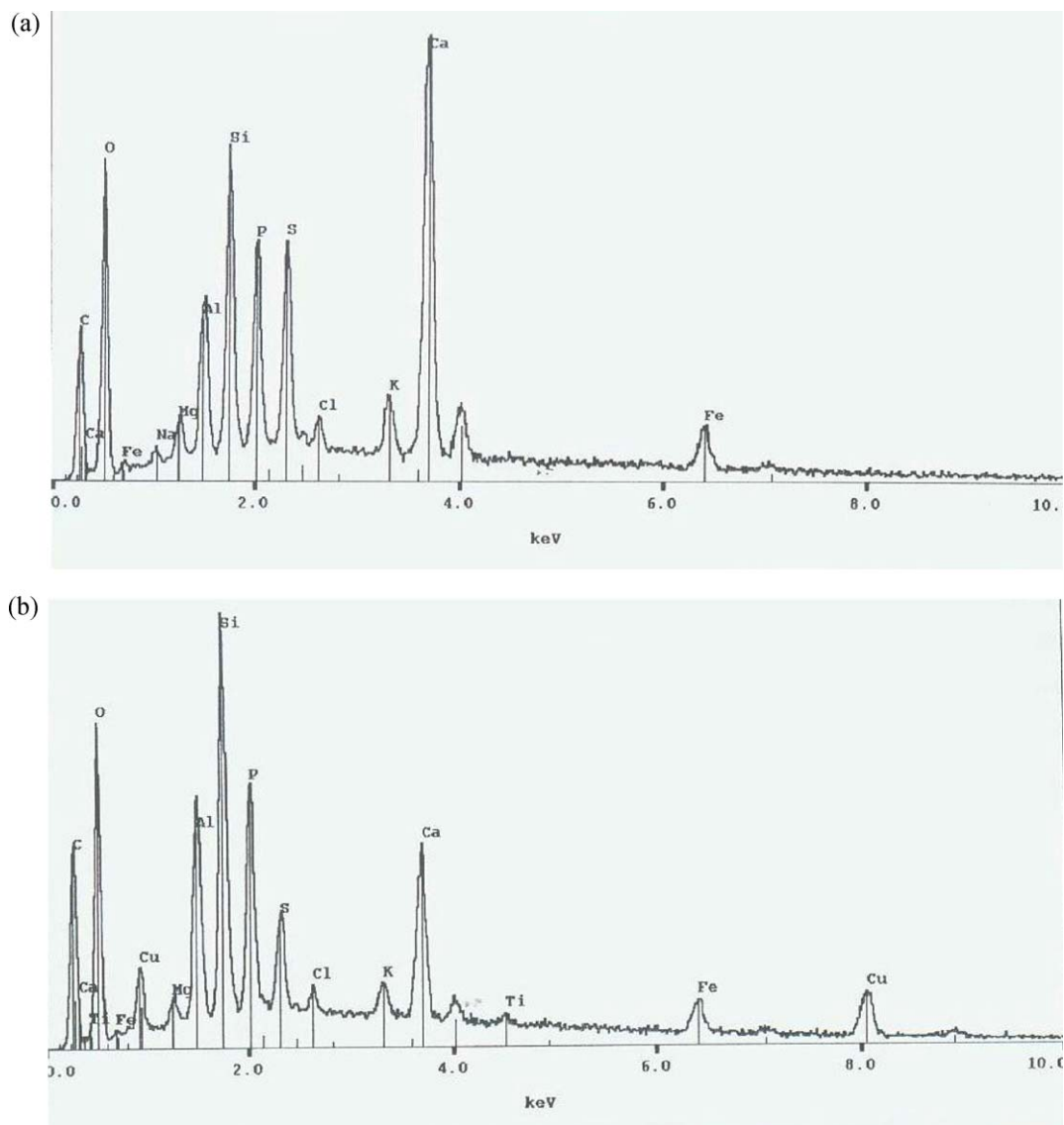
Fig. 8. EDAX spectra of dried activated sludge: (a) in the absence of copper and (b) after copper biosorption (C_0 = 100 ppm).

3.3. Scanning electron microscopy/energy dispersive analysis of X-rays (SEM/EDAX)

Electron microscopic examination of dried activated sludge, before and after copper biosorption, was also undertaken in order to locate the active sorptive sites of the biosorbent. The scanning electron microscopic (SEM) micrographs and the X-ray energy dispersion analysis (EDAX) of dried activated sludge, before and after equilibration with copper solution, are shown in Figs. 7a, b and 8a, respectively.

The SEM micrograph (see Fig. 7a) shows the presence of white nodules indicating the presence of heavy elements such as: calcium, etc. Their EDAX analysis conclusively identified them as: Al, Si, P, S, Cl, K, Ca and Fe, with no copper signal presence (see Fig. 8a): copper is not present superficially in the dried activated sludge structure. Dried activated sludge contains both inorganic and organic matters, mainly in the forms of iron, alumina, silica and carbonates. The presence of white nodules is more clear in Fig. 7b in which dried activated sludge had been exposed to 100 ppm copper solution. The EDAX spectrum of these nodules showed a copper signal and other elements signals observed previously, as illustrated in Fig. 8b. The presence of cadmium on

sunflower leaves is consistent with the uptake isotherm. The analysis results confirm in the biosorption of copper by dried activated sludge, the metal is mainly located superficially in the biosorbent structure.

4. Conclusion

The results obtained confirm that dried activated sludge can remove copper ions from aqueous solution. The sorption kinetics performances are strongly affected by parameters such as: contact time, initial copper concentration and initial pH of solution. The amount of copper removed by dried activated sludge increased with the increase of these parameters at a specific time. The kinetics of copper biosorption followed a pseudo-second-order rate kinetics. Analysis of diffusion mechanisms of copper biosorption by dried activated sludge was problematic: diffusion mechanisms were predominant in rate controlling steps. The investigated operating parameters have different effects on mass transfer coefficients. Under these experimental conditions, the analysis of mechanistic steps involved in the copper biosorption process confirms that the biosorption process is particle-diffusion-controlled, with some pre-

dominance of some external mass transfer at the initial stages. An acceptable fitting of the equilibrium isotherm was obtained with Langmuir model in all the range of copper concentrations studied. Electron micrographs obtained show that copper is present superficially in dried activated sludge. The analysis results confirm the biosorption of copper by dried activated sludge. This experimental study is quite useful in developing an appropriate technology for designing a waste water treatment plant. However, further work should be performed in order to better understand copper biosorption binding mechanism by dried activated sludge.

Acknowledgements

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