

Batch kinetics and isotherms for biosorption of copper(II) ions onto pre-treated powdered waste sludge (PWS)

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Abstract

Waste sludge samples from different plants were tested for Cu(II) ion biosorption capacities with and without pre-treatment. Waste sludge from a paint industry wastewater treatment plant was found to perform better than the others after pre-treatment with 1% H₂O₂. Powdered waste sludge (PWS) from the paint industry wastewater treatment plant was used for recovery of Cu(II) ions from aqueous solution by biosorption after pre-treatment with 1% H₂O₂. Batch kinetics and isotherms of biosorption of Cu(II) ions were investigated at variable initial Cu(II) concentrations between 50 and 400 mg l⁻¹ with a PWS particle size of 64 μm. The pseudo-first and -second order kinetic models were used to correlate the experimental data. The kinetic constants were determined for both models and the second order kinetic model was found to be more suitable. The Langmuir, Freundlich and the generalized isotherm models were used to correlate the equilibrium biosorption data and the isotherm constants were determined. The Langmuir isotherm was found to fit the experimental data better than the other isotherms tested. The maximum biosorption capacity (116 mg g⁻¹) of the pre-treated powdered waste sludge for Cu(II) ions was found to be superior as compared to the other biosorbents reported in literature

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1. Introduction

Presence of heavy metals in some chemical industry wastewaters such as pulp and paper, petrochemicals, refineries, fertilizers, steel and automobile industries adversely affect the performance of biological treatment systems and also cause considerable toxic effects on the receiving environment [1–5]. For this reason, removal and recovery of heavy metals from industrial wastewaters before biological treatment has gained significant attention in recent years. Copper, zinc, lead, mercury, chromium, cadmium, cobalt, nickel and mercury are the most frequently found heavy metals in industrial wastewaters [1].

Uncontrolled discharge of heavy metal containing wastewaters to the environment can be detrimental to humans, animals and the plants. Different methods were developed for removal of heavy metals from wastewater [2,3]. Chemical methods such

as precipitation, adsorption, ion exchange, and solvent extraction require high capital and operating costs and may produce large volumes of solid wastes [2–4]. Recent research efforts were concentrated on recovery of heavy metals using different biomaterials such as waste sludge, digested sludge, and waste biomass from commercial bioprocesses [5–24]. Because of negative surface charge and membrane compositions, organisms (bacteria, yeast, molds, fungi) are natural adsorbents for metal ions. The excess activated sludge provides an excellent opportunity for removal of heavy metals by biosorption because of its availability and free use [5]. Biosorption is essentially the passive and physicochemical binding of chemical species or ions to biopolymers on the surfaces of organisms [6,7]. Some advantages of biosorption for removal of heavy metals over chemical and physical methods are: (a) excess sludge from wastewater treatment plants may be used as biosorbent, (b) low cost, free availability and possible reuse of the biosorbent, (c) high biosorption capacity because of large surface area of sludge organisms, and (d) selective adsorption of metal ions.

Large number of studies were reported in literature on biosorption of heavy metals onto different organisms [5–24].

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Most of those studies were done using pure cultures of bacteria, yeasts and molds [7–13]. However, activated sludge organisms in form of live or dead were also used for biosorption of heavy metal ions by different investigators using different types of reactors [14–24].

In none of the literature studies biosorption of Cu(II) ions onto pre-treated powdered waste sludge (PWS) was studied extensively. Since copper(II) ions are commonly present in metal industry effluents, it was selected as the model metal ion. Activated sludge samples from different wastewater treatment plants were tested and the sludge from a paint industry wastewater treatment plant was used for biosorption of Cu(II) ions because of its high biosorption capacity. The powdered waste sludge (PWS) was pre-treated with 1% H₂O₂ to improve the biosorption capacity since pre-treatment with 1% H₂O₂ resulted in better biosorption performance as compared to the other pre-treatment solutions. The pre-treated PWS was ground, sieved to different particle sizes and used for biosorption of Cu(II) ions from solution. The kinetics and isotherms of the biosorption was investigated by varying the initial Cu(II) concentration using PWS with an average particle size of 64 μm. Biosorption isotherms were established by using the equilibrium data and the isotherm constants were determined.

2. Materials and methods

2.1. Experimental system

Batch shake flask experiments were performed using a gyratory shaker at 150 rpm and room temperature (25 °C). Erlenmeyer flasks of 500 ml were charged with 200 ml of tap water. Cu(II) ions (in form of CuSO₄) and PWS were added to the flasks to yield desired concentrations of Cu(II) (50–400 mg l⁻¹) and 1 g l⁻¹ PWS in the solution. In activated sludge selection experiments with and without pre-treatment the PWS and Cu(II) concentrations were 1 g l⁻¹ and 100 mg l⁻¹, respectively. The pH was adjusted to 5 in all experiments since pH 5 was reported to be the optimum pH for copper biosorption [19,20,25,26] and also to avoid Cu(II) precipitation in form of Cu(OH)₂ at pH levels above 5 [25]. The flasks were incubated in a gyratory shaker (Gallenkamp) at 25 °C for 24 h. Samples were removed from the flasks every hour for analysis. A control flask free of PWS with 100 mg l⁻¹ Cu(II) ions was used to determine Cu(II) removal in the absence of the adsorbent.

2.2. Experimental procedure

Five activated sludge samples were obtained from different wastewater treatment plants. Two samples were from industrial treatment plants (PAK MAYA Bakers yeast and DYO paint companies). The other two samples were from domestic (Guzelbahce and Kissikoy) and one sample from municipal wastewater treatment plant (Cigli) in Izmir, Turkey. The samples were dried at 80 °C until constant weight, ground and sieved below –70 mesh ($D_p < 212 \mu\text{m}$) before use in adsorption experiments. Waste activated sludge samples obtained from different wastewater treatment plants were tested for their Cu(II) ion

biosorption capabilities without pre-treatment and the sludge obtained from DYO paint industry in Izmir, Turkey was found to be superior to the other sludges tested. The raw sludge from the paint industry contained 16 μg l⁻¹ Cr, 58 μg l⁻¹ Zn, 2 μg l⁻¹ Cu, 1 μg l⁻¹ Pb, 80 μg l⁻¹ Fe, 20 μg l⁻¹ Mn, and no detectable Ni and Cd with a density of 1.2 g cm⁻³. The selected sludge was dried, ground and sieved to desired particle size before use in biosorption experiments. Due to low biosorption capacity of the untreated powdered waste sludges (PWS), the PWS samples were pre-treated using five different pre-treatment solutions: 1% H₂SO₄, NaOH, ethanol, NaOCl and H₂O₂. Pre-treatment solution of 200 ml was mixed with 2 g of PWS in a 500 ml erlenmeyer flask and placed on a gyratory shaker (Gallenkamp) at 150 rpm and 25 °C for 6 h. Pre-treated PWS was washed with deionized water on a blue-ribbon filter paper until the filtrate pH was neutral. Pre-treated and washed PWS samples were dried at 80 °C, reground and sieved to different mesh sizes. Only the size fraction between 200 and 270 mesh with an average particle size of 64 μm was used in kinetic and isotherm studies reported in this article. The BET surface area of dried sludge with a particle size of 64 μm was 69 m² g⁻¹ after pre-treatment with 1% H₂O₂.

2.3. Analytical methods

The samples (5 ml) withdrawn from the erlenmeyers every hour were centrifuged at 8000 rpm (7000 × g) to remove solids. The clear supernatants were analyzed for copper(II) contents using an atomic absorption spectrometer (ATI Unicam 929 AA Spectrometer) at 324.8 nm wavelength.

3. Theoretical background

Two different kinetic models were used for correlation of biosorption data. The pseudo-first order kinetic model [27,28] has the following form:

$$\ln(1 - q/q_e) = -k_1 t \quad \text{or} \quad q = q_e(1 - \exp(-k_1 t)) \quad (1)$$

where q and q_e are the solid phase Cu(II) concentrations at any time (t) and at the equilibrium (mg g⁻¹), respectively, and k_1 is the first order rate constant (h⁻¹). When the experimental data was plotted in form of $\ln(1 - q/q_e)$ versus time, a straight line would be obtained if the pseudo-first order kinetic model is a suitable expression. The rate constant (k_1) is obtained from the slope of the line.

The pseudo-second order kinetic model as developed by Ho and McKay [27,28] has the following form:

$$t/q = 1/(k_2 q_e^2) + t/q_e \quad (2)$$

where k_2 is the pseudo-second order rate constant ((mg/g)⁻¹ h⁻¹). When t/q was plotted against time a straight line would be obtained if the second order model is a suitable expression. The second order rate constant (k_2) is obtained from the y-axis intercept of the line.

Three different biosorption isotherms namely the Langmuir, Freundlich and the generalized biosorption isotherms were used to correlate the equilibrium biosorption data [16,17,24,26].

Langmuir isotherm has the following form:

$$q_e = X/M = q_m C_e / (K + C_e) \quad (3)$$

which may be written in linearized form as follows:

$$1/q_e = 1/q_m + (K/q_m)1/C_e \quad (4)$$

where X is the amount of Cu(II) removed from solution by biosorption ($V(C_0 - C)$, mg); M the amount of biosorbent (PWS) used (g); q_e the equilibrium biosorbed Cu(II) concentration in the solid phase (mg g^{-1}); q_m the maximum biosorption capacity of the adsorbent for Cu(II) ions (mg g^{-1}); C_e the aqueous phase equilibrium concentration of the Cu(II) ions (mg l^{-1}) and K is the saturation constant (mg l^{-1}). A plot of $1/q_e$ versus $1/C_e$ yields a straight line if the Langmuir isotherm is a suitable expression.

Freundlich isotherm has the following form:

$$q_e = K C_e^{1/n} \quad (5)$$

or in linearized form Eq. (5) can be written as

$$\ln q_e = \ln K + (1/n) \ln C_e \quad (6)$$

where K is the Freundlich capacity constant ($\text{mg g}^{-1} (\text{mg l}^{-1})^{-1/n}$); n the affinity constant; q_e the equilibrium biosorbed Cu(II) ion concentration in the solid phase (mg g^{-1}) and C_e is the equilibrium Cu(II) ion concentration in aqueous phase (mg l^{-1}). A plot of $\ln q_e$ versus $\ln C_e$ would yield a straight line if the Freundlich isotherm is a suitable expression.

The third isotherm tested for correlation of the equilibrium data was the generalized biosorption isotherm equation which has the following form:

$$q_e = q_m C_e^n / (K + C_e^n) \quad (7)$$

Eq. (7) can be written as follows in linearized form:

$$\ln((q_m/q_e) - 1) = \ln K - n \ln C_e \quad (8)$$

where K is the saturation constant ($(\text{mg l}^{-1})^{-n}$); n is the cooperative binding constant; q_m the maximum biosorption capacity of the adsorbent (mg g^{-1}); q_e (mg g^{-1}) and C_e (mg l^{-1}) are the equilibrium Cu(II) ion concentrations in the solid and aqueous phases, respectively. A plot of the equilibrium data in form of $\ln((q_m/q_e) - 1)$ versus $\ln C_e$ would yield a straight line if the generalized adsorption isotherm is valid.

4. Results and discussion

4.1. Selection of PWS and the pre-treatment method

The results of the experiments for selection of the most suitable waste sludge (PWS) and pre-treatment method are summarized in Fig. 1 in form of bar diagrams. Percent copper ion removals by biosorption are depicted for different activated sludge samples and pre-treatment methods. Industrial sludges from Pak Maya Bakers Yeast and DYO paint companies treatment plants performed much better than those from domestic and municipal treatment plants. Since the industrial sludges were exposed to heavy metals in the treatment plants, their biosorption

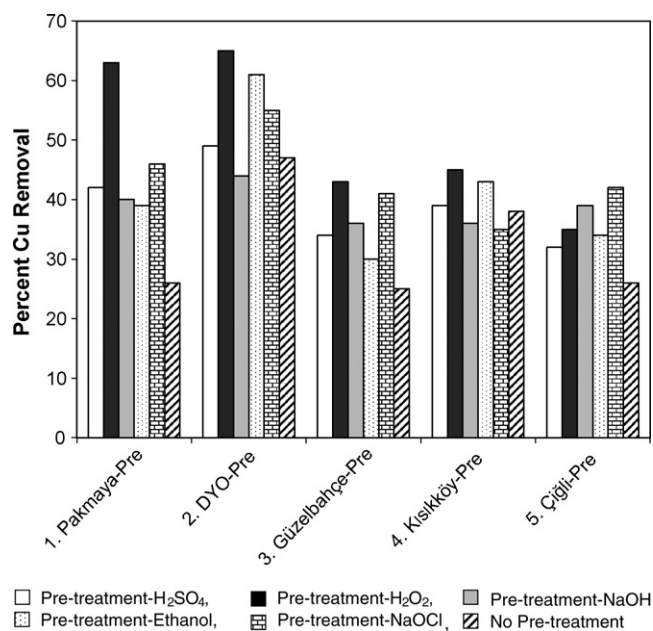


Fig. 1. Variation of percent copper ion removal by biosorption for different PWS samples with different pre-treatment methods. PWS 1 g l^{-1} , Cu_0 100 mg l^{-1} , pH 5.

capacities were higher as a result of adaptation. Also, the composition of microbial flora in industrial wastewater treatment plants may be more suitable for heavy metal biosorption as compared to the domestic sludges. The highest percent copper removal (65%) was obtained by using PWS from DYO paint industry treatment plant after pre-treatment with 1% H_2O_2 . PWS from PAK MAYA Bakers yeast treatment plant yielded 63% copper ion removal when pre-treated with 1% H_2O_2 . Therefore, the most suitable sludge and pre-treatment methods were the sludge from DYO paint company and the pre-treatment with 1% H_2O_2 . Probably H_2O_2 oxidized or activated some functional groups on the surfaces of bacterial biomass and provided more suitable surface characteristics for attachment of copper ions. Zeta potential on the surfaces of PWS decreased to -15.6 mV after pre-treatment with 1% H_2O_2 at pH 5 which increased attraction of Cu(II) ions onto PWS surfaces [25].

4.2. Kinetic studies

The kinetics of biosorption of Cu(II) onto pre-treated PWS were investigated for different initial Cu(II) concentrations varying between 50 and 400 mg l^{-1} with the PWS concentration of 1 g l^{-1} and particle size of $64 \mu\text{m}$. Fig. 2 depicts variation of biosorbed Cu(II) concentrations with time for different initial Cu(II) concentrations. Solid phase Cu(II) concentration increased with time and reached an equilibrium after 6 h of incubation for all cases. Biosorbed copper concentrations also increased with increasing initial Cu(II) concentrations yielding the highest q_e value of $116 \text{ mg Cu g PWS}^{-1}$ at initial Cu(II) concentration of 400 mg l^{-1} . At low Cu(II) concentrations, the extent of biosorption was limited by the availability of Cu(II) ions yielding low solid phase Cu(II) concentrations at equilibrium. As the initial Cu(II) concentrations increased, larger

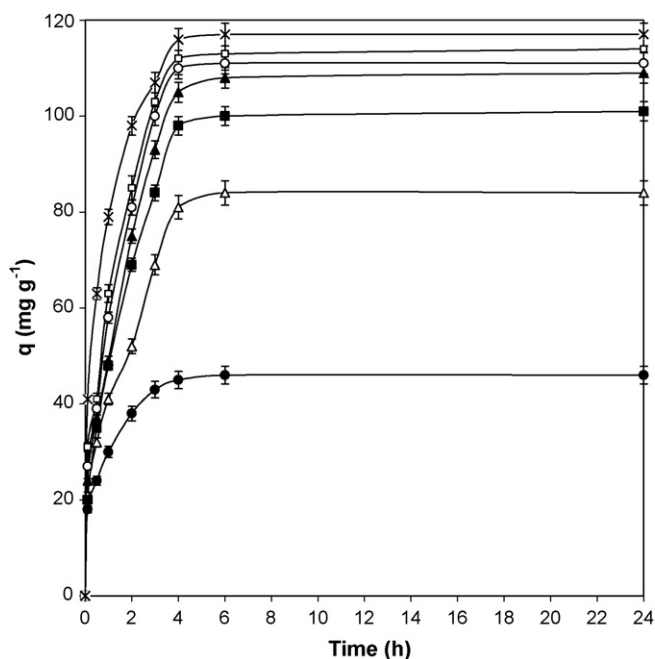


Fig. 2. Variation of biosorbed copper ion concentration with time for different initial copper ion concentrations. Cu_0 ($mg\ l^{-1}$): ●: 50, △: 100, ■: 150, ▲: 200, ○: 250, □: 300, *400. PWS $1\ g\ l^{-1}$, D_p $64\ \mu m$, pH 5.

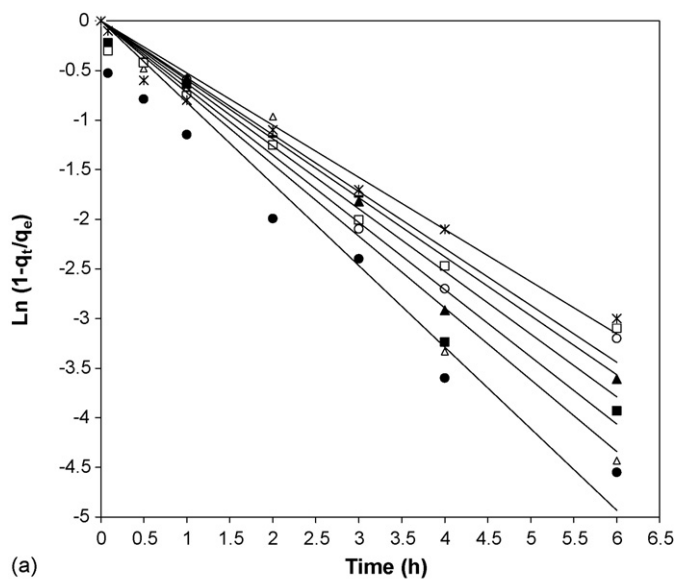
fractions of Cu(II) ions were adsorbed onto PWS surfaces yielding high biosorbed copper concentrations.

Both the pseudo-first and -second order kinetic models were used to correlate the experimental data. Experimental data were plotted in form of $\ln(1 - q/q_e)$ in Fig. 3a to test the validity of the pseudo-first order model. The kinetic constants for the pseudo-first order model were determined from the slopes of the lines in Fig. 3a. Fig. 3b depicts plots of t/q versus time for different initial Cu(II) concentrations to test the suitability of the second order kinetic model where the rate constants (k_2) were determined from the y-axis intercepts of the lines according to Eq. (2). Pseudo-second order kinetic model was found to be more suitable for representation of the experimental data due to larger correlation coefficients as compared to the first order kinetic model.

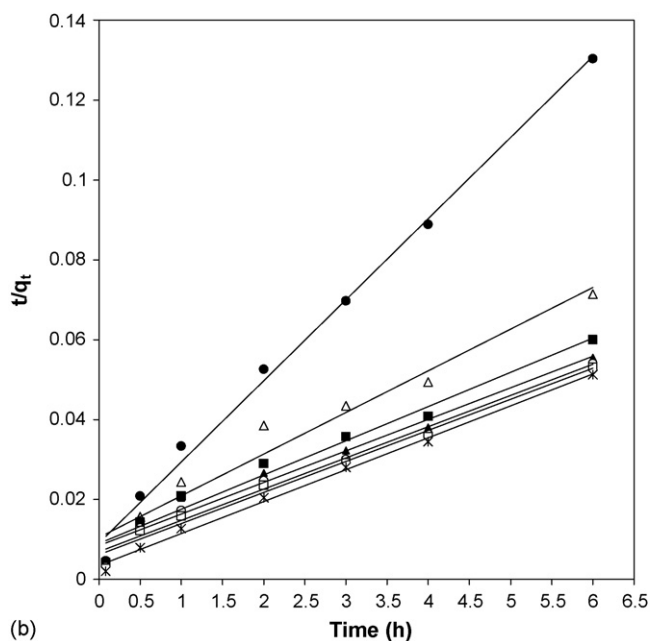
Variations of the pseudo-first and -second order rate constants with initial Cu(II) concentration are summarized in Table 1. The rate constants for both the pseudo-first and -second order models decreased with increasing initial Cu(II) concentrations. The first and second order rate constants decreased from $0.822\ h^{-1}$ and

Table 1
Variation of the pseudo-first and -second order rate constants with initial Cu(II) concentrations

R^2	K_2 (mg/g) $^{-1}\ h^{-1}$	R^2	K_1 (h^{-1})	Cu(II) $mg\ l^{-1}$
0.99	0.0591	0.95	0.822	50
0.96	0.0232	0.93	0.724	100
0.97	0.0136	0.94	0.6772	150
0.98	0.0113	0.95	0.6317	200
0.96	0.0110	0.94	0.5942	250
0.96	0.0109	0.96	0.5735	300
0.99	0.0100	0.97	0.5254	400



(a)



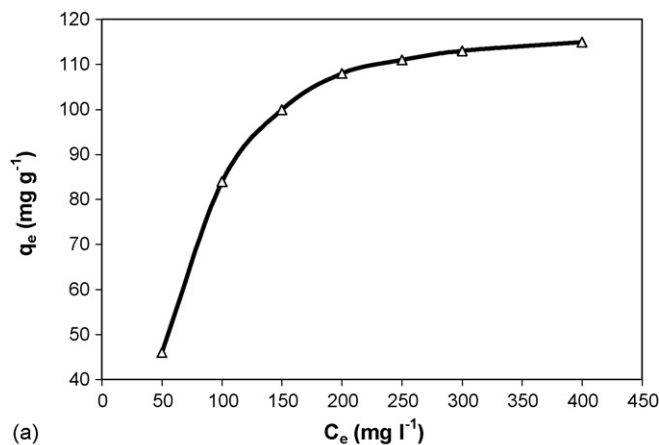
(b)

Fig. 3. (a) A plot of $\ln(1 - q_t/q_e)$ vs. time for the pseudo-first order biosorption kinetics; (b) a plot of t/q vs. time for the second order biosorption kinetics. Cu ($mg\ l^{-1}$): ●: 50, △: 100, ■: 150, ▲: 200, ○: 250, □: 300, *: 400 $mg\ l^{-1}$. PWS = $1\ g\ l^{-1}$, pH 5, $D_p = 64\ \mu m$.

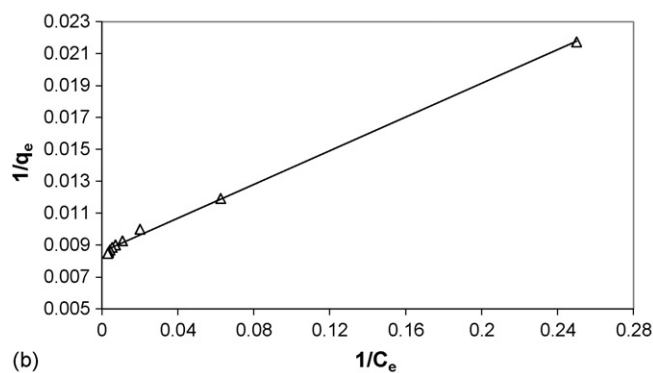
$0.059\ (mg/g)^{-1}\ h^{-1}$ to $0.525\ h^{-1}$ and $0.010\ (mg/g)^{-1}\ h^{-1}$ when the Cu(II) concentration increased from 50 to 400 $mg\ l^{-1}$. The reason for the decrease in the rate constant with increasing Cu(II) concentrations may be the competition among copper ions for the same binding sites on PWS surfaces.

4.3. Isotherm studies

The plots of equilibrium concentrations of Cu(II) ions in the solid and aqueous phases, that is q_e versus C_e and also $1/q_e$ versus $1/C_e$ are presented in Fig. 4a and b, respectively. From the slope and intercept of the line in Fig. 4b, the Langmuir constants were



(a)



(b)

Fig. 4. (a) Variation of equilibrium biosorbed Cu(II) ion concentration with the equilibrium aqueous phase Cu(II) concentration. (b) Langmuir isotherm plot of $1/q_e$ vs. $1/C_e$. PWS 1 g l^{-1} , D_p $64 \mu\text{m}$, pH 5.

found as

$$q_m = 116.3 \text{ mg g}^{-1}, \quad K = 6.14 \text{ mg l}^{-1} \quad (R^2 = 0.998)$$

Apparently, equilibrium biosorption data of Cu(II) ions fit to the Langmuir isotherm very well ($R^2 = 0.998$). In fact, the hyperbolic shape of the graph (q_e versus C_e) in Fig. 4a also indicated that the Langmuir isotherm represented the equilibrium data quite well.

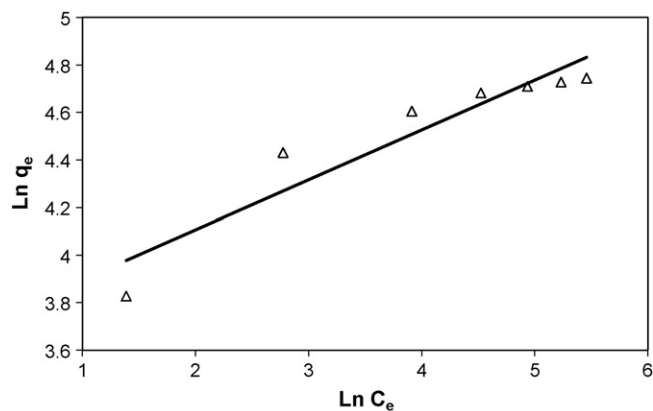


Fig. 5. Freundlich isotherm plot of $\ln q_e$ vs. $\ln C_e$ for biosorption of Cu(II) ions onto pre-treated PWS. PWS 1 g l^{-1} , D_p $64 \mu\text{m}$, pH 5.

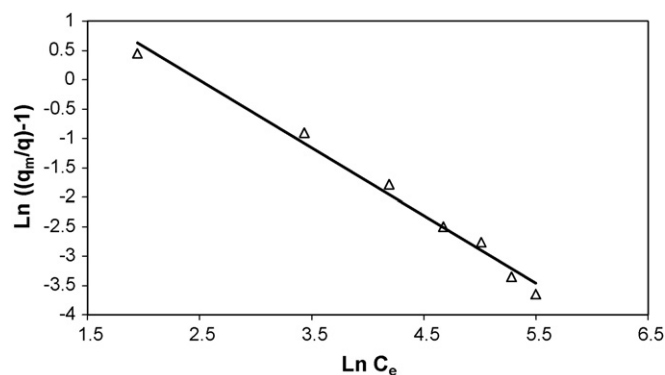


Fig. 6. Generalized biosorption isotherm plot of $\ln((q_m/q_e) - 1)$ vs. $\ln C_e$ for Cu(II) ion biosorption onto PWS. PWS 1 g l^{-1} , D_p $64 \mu\text{m}$, pH 5.

Fig. 5 depicts a plot of $\ln q_e$ versus $\ln C_e$ for Cu(II) ion biosorption onto the PWS. From the slope and intercept of the line, the following Freundlich isotherm constants were found:

$$K = 40 \text{ mg g}^{-1} (\text{mg l}^{-1})^{1/n},$$

$$1/n = 0.21, \quad (n = 4.76) \quad (R^2 = 0.89)$$

Apparently, the Freundlich isotherm did not represent the equilibrium data as well as the Langmuir isotherm.

A plot of the equilibrium data in form of $\ln((q_m/q_e) - 1)$ versus $\ln C_e$ is depicted in Fig. 6. The q_m value was taken as $q_m = 116.3 \text{ mg g}^{-1}$ as determined from the Langmuir isotherm. From the slope and intercept of the line presented in Fig. 6, the following values were found for the constants of the generalized biosorption isotherm:

$$K = 17.65 (\text{mg l}^{-1})^n, \quad n = 1.152 \quad (R^2 = 0.987)$$

Apparently, the generalized adsorption isotherm represents the equilibrium data reasonably well, but the fit is not as good as the Langmuir isotherm. Since the exponent (n) was close to 1 ($n = 1.15$), the generalized isotherm approximates to the Langmuir expression.

Table 2 summarizes the results of the isotherm constants for the three different equilibrium isotherms tested. On the basis of the correlation coefficients (R^2), Langmuir isotherm seemed to represent the equilibrium adsorption data with better fit as compared to the other isotherms. However, the generalized isotherm was also satisfactory for representation of the equilibrium data.

As compared to the literature studies on biosorption of copper(II) ions onto waste activated sludge [15,20,23,26] the maximum biosorption capacity (q_m) obtained in this study

Table 2

Summary of the isotherm constants and the correlation coefficients for different isotherms

Parameter	Langmuir isotherm	Freundlich isotherm	Generalized isotherm
q_m (mg g^{-1})	116.3		116.3
K	6.14	40.0	17.65
n		4.76	1.152
R^2	0.998	0.89	0.987

(116 mg g⁻¹) is superior to the literature values which vary between 10 and 80 mg g⁻¹. The saturation constant for the Langmuir isotherm ($K = 6.14 \text{ mg l}^{-1}$) is also considerably lower than those reported in literature on copper biosorption [23] indicating high affinity of the waste sludge used for Cu(II) biosorption. This is probably because of the selection of a better waste sludge, pre-treatment with 1% H₂O₂ and also the small particle size (64 μm) of PWS used in this study.

5. Conclusions

Five waste activated sludge samples from different wastewater treatment plants were tested for their Cu(II) ion adsorption capabilities with and without pre-treatment. The sludge from DYO paint industry wastewater treatment plant was found to perform better than the others tested. Among the five different pre-treatment solutions 1% H₂O₂ was found to be superior to the others yielding higher Cu(II) biosorption capacity. Using the waste sludge from the paint industry after pre-treatment with 1% H₂O₂, kinetics and isotherms of biosorption of Cu(II) ions onto pre-treated powdered waste sludge (PWS) was studied. Experiments were carried out by varying initial Cu(II) ion concentrations between 50 and 400 mg l⁻¹ while the adsorbent (PWS) concentration and the particle size were constant at 1 g l⁻¹ and 64 μm at pH 5. Pseudo-first order and -second order kinetic models were used to correlate the pre-equilibrium biosorption data and the kinetic constants were determined for both models. Pseudo-second order kinetic model represented the data better than the first order model for biosorption of Cu(II) ions onto PWS. Three different biosorption isotherms namely the Langmuir, Freundlich and the generalized isotherms were used to correlate the equilibrium experimental data. The constants of each isotherm were determined by using the equilibrium biosorption data. The Langmuir isotherm was found to fit the experimental data better than the other isotherms tested although the generalized isotherm also represented the data reasonably well. The maximum biosorption capacity of pre-treated PWS for the Cu(II) ions was found to be nearly 116.3 mg Cu gPWS⁻¹. The paint industry waste sludge used for Cu(II) ion biosorption was found to be superior to the waste sludges used by other investigators yielding higher biosorption capacity (q_m) and lower saturation constant (K) for the Langmuir isotherm.

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