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Cu(II) Ion Recovery by Biosorption onto Powdered Waste Sludge (PWS) in a Fed-Batch Reactor: Particle Size Effects

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Abstract: Biosorption of Cu(II) ions onto pre-treated powdered waste sludge (PWS) was investigated using a completely mixed reactor operating in fed-batch mode. Experiments were performed with PWS of different particle sizes between 53 and 231 μm while the feed flow rate ($0.25\,l\,h^{-1}$), feed copper ion concentrations ($200\,mg\,l^{-1}$) and the amount of adsorbent (2 g PWS) were constant. Breakthrough curves describing variations of the aqueous phase copper ion concentrations with time were determined for different particle sizes of the adsorbent. Percent copper removal from the aqueous phase and the biosorbed copper ion concentrations increased with decreasing particle size or increasing surface area of the PWS. A modified Bohart-Adams equation was used to determine the biosorption capacity of PWS and the rate constant for Cu(II) ion biosorption. The biosorption capacity of PWS based on per unit mass of PWS (g Cu $gPWS^{-1}$) increased with decreasing particle size due to increased external surface area of PWS. The biosorption capacity of PWS for Cu(II) ions in completely mixed fed-batch reactor was found to be comparable with the powdered activated (PAC) adsorption columns However, the adsorption rate constant in a completely mixed fed-batch reactor was an order of magnitude larger than those obtained in adsorption columns because of the elimination of mass transfer limitations encountered in the column operations. Therefore, it was proven that the adsorption capacity and the rate of adsorption can be improved by reducing the particle size of the adsorbent (PWS) and using a completely mixed

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fed-batch reactor due to a larger adsorbent surface area and better contact between the phases.

Keywords: Biosorption, copper (II) ions, fed-batch reactor, powdered waste sludge (PWS)

INTRODUCTION

Adverse effects of heavy metal ions present in some chemical industry wastewaters such as pulp and paper, petrochemicals, refineries, fertilizers, steel, and automobile industries on the performance of biological treatment systems and on the receiving environment have been observed and reported by many investigators (1–4). Uncontrolled discharge of heavy metal containing wastewaters to the environment can be detrimental to humans, animals, and plants. As a result, the removal and recovery of heavy metals from industrial wastewaters before biological treatment has gained significant attention in recent years to protect the environment. Lead, mercury, chromium, cadmium, copper, zinc, nickel, and cobalt are the most frequently found heavy metals in industrial wastewaters (1).

The methods used for the removal of heavy metals from wastewaters can be classified as physical, chemical, and biological methods (2–3). Physical-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). Utilization of different biomaterials such as waste sludge, digested sludge, and waste biomass as adsorbent offers special advantages for recovery of heavy metals (5–11). Because of negative surface charge and membrane compositions, organisms (bacteria, yeast, molds, fungi) may be used as natural adsorbents for metal ions. The excess activated sludge provides an excellent opportunity for removal of heavy metals by biosorption because of its availability on the plant site and free use. Some advantages of biosoption of heavy metals onto waste sludge can be summarized as follows (2, 4):

1. Excess sludge from wastewater treatment plants may be used as biosorbent
2. Low cost and free availability of the biosorbent
3. High biosorption capacity because of a large surface area of sludge organisms
4. Selective adsorption of metal ions because of negative surface charge of the sludge
5. Operation over a broad range of environmental conditions

Numerous studies were reported in the literature on biosorption of heavy metals onto different organisms. Most of the reported studies were done

using pure cultures of bacteria, yeasts, and molds to determine the metal ion biosorption capacity and equilibrium isotherms for different types of organisms (7–13). A number of studies were reported on the use of activated sludge organisms or dried waste sludge for removal of heavy metal ions from aqueous solutions over the last ten years (14–24). Aerobic or anaerobic waste sludge were used for the removal of single or a mixture of metal ions in batch systems to determine the biosorption capacities, kinetics, and equilibrium isotherms.

Most of the large scale adsorption operations are realized in adsorption columns because of easy operation and separated solid adsorbent and the aqueous phases. However, due to the heterogenous nature of adsorption columns it is difficult to control the environmental conditions such as pH, ion concentrations, uniform flow, and effective contact between the phases. Therefore, flow channeling, transport limitations, and a limited contact area between the phases result in some unexpected anomalies in the performance of adsorption columns. The rate of adsorption is usually low due to transport limitations in adsorption columns requiring large volumes of columns.

As an alternative to column operations, a completely mixed reactor operated in fed-batch mode was used in this study for removal of Cu(II) ions from aqueous solution by adsorption on pre-treated powdered waste sludge (PWS). Fed-batch operation of completely mixed adsorption reactors have the following advantages over the adsorption columns.

1. Provides better contact between the adsorbent and the adsorbate since the adsorbent particles are not in contact with each other due to complete mixing
2. Reduces transport limitations (liquid film resistance) encountered in adsorption columns to a minimum level
3. Improves the rate of adsorption due to complete mixing and better contact between the phases
4. Provides a homogenous mixture and therefore, better control of the environmental conditions (pH, adsorbent and adsorbate concentrations, hydrodynamical conditions)
5. Eliminates hydrodynamical problems such as flow channeling, dead regions, radial dispersion encountered in adsorption columns.

No reports were found in the literature on the use of fed-batch reactors for adsorption with a sedimentation period. Therefore, the major goal of this study is to investigate the biosorption of Cu(II) ions onto pre-treated powdered waste sludge (PWS) in a completely mixed reactor operating in fed-batch mode. The effects of the particle size of the adsorbent (PWS) on Cu(II) ion removal performance of the system was investigated while the feed Cu(II) concentration ($200\ mg\ l^{-1}$), feed flow rate ($0.25\ l\ h^{-1}$), and the mass of adsorbent (PWS, 2 g) was constant. The data were used to establish the

break-through curves where break-through times were determined to reach a certain effluent adsorbate (copper ion) concentration. A modified Bohart-Adams equation (25, 26) was used to estimate the mass and surface adsorption capacity of the PWS and also the rate constant.

THEORETICAL BACKGROUND

The Bohart-Adams equation used for the design of adsorption columns was modified for fed-batch operation. Since no effluent was removed from the completely mixed reactor operated in fed-batch mode, the volume of the liquid in the reactor increased with time until the reactor was full.

According to the Bohart–Adams model (25, 26), the following equation is used to predict the performance of adsorption columns:

$$t_b = \frac{N_o X}{C_o V_o} - \frac{1}{K C_o} \mathrm{Ln}\left[\frac{C_o}{C_b} - 1\right] \tag{1}$$

where, t_b is the operation time to reach the break-through concentration C_b in the effluent (h), C_o is the adsorbate (feed copper(II) ion) concentration (kg m^{-3}), C_b is the effluent adsorbate concentration at the break-through point (kg m^{-3}), N_o is the adsorption capacity of the adsorbent per unit bed volume (kg adsorbate $\cdot$ m^{-3} of bed), X is the depth of the packed section of the column (m), V_o is the linear velocity of fluid (Q/A, m h^{-1}), K is the adsorption rate constant (m^3 $kg^{-1} \cdot h^{-1}$). The following definitions were used to modify Eqn. (1).

$$N_o = q_s(1 - \varepsilon) \tag{2}$$

$$V_{bed} = XA_o = \frac{V_{ads}}{(1 - \varepsilon)} \tag{3}$$

where, q_s is the capacity of the adsorbent per unit adsorbent volume (kg adsorbate $\cdot$ m^{-3} adsorbent), $(1 - \varepsilon)$ is the adsorbent (solid) volume fraction (m^3 adsorbent $\cdot$ m^{-3} bed) in the reactor or in the bed, A_o is the cross section area of bed (m^2), and V_{ads} is the volume of the adsorbent in the reactor or in the bed (m^3). The Bohart–Adams equation takes the following form after substitution of Eqns. (2) and (3) into Eqn. (1) and multiplying and dividing the first term by A_o.

$$t_b = \frac{q_s(1 - \varepsilon)}{C_o V_o A_o}(XA_o) - \frac{1}{K C_o} \mathrm{Ln}\left[\frac{C_o}{C_b} - 1\right] \tag{4}$$

Further arrangement yields,

$$t_b = \frac{q_s(1 - \varepsilon)}{C_o Q} \frac{V_{ads}}{(1 - \varepsilon)} - \frac{1}{K C_o} \mathrm{Ln}\left[\frac{C_o}{C_b} - 1\right] \tag{5}$$

where Q is the volumetric flow rate of the feed solution (m^3 h^{-1}).

Adsorbent volume is defined as

$$V_{ads} = \frac{m_{ads}}{\rho_{ads}} \tag{6}$$

Substitution of Eqn. (6) into Eqn. (5) yields,

$$t_b = \frac{q_s}{C_o Q}\frac{m_{ads}}{\rho_{ads}} - \frac{1}{KC_o}\mathrm{Ln}\left[\frac{C_o}{C_b} - 1\right] \tag{7}$$

where, m_{ads} is mass of the adsorbent (kg), ρ_{ads} is the density of dry adsorbent (kg adsorbent $\cdot$ m^{-3} adsorbent).

By defining the capacity of the adsorbent per unit mass of adsorbent (q_s') as follows

$$q_s' = \frac{q_s}{\rho_{ads}} \tag{8}$$

where q_s' is the adsorption capacity per unit mass of adsorbent (kg adsorbate $\cdot$ kg^{-1} adsorbent), one can write Eqn. (7) as follows

$$t_b = \frac{q_s'}{C_o Q} m_{ads} - \frac{1}{KC_o}\mathrm{Ln}\left[\frac{C_o}{C_b} - 1\right] \tag{9}$$

where QC_o/m_{ads} is the specific loading rate of solute (adsorbate) per unit mass of adsorbent (L_s = kg adsorbate kg^{-1} adsorbent $\cdot$ h^{-1}) which is inversely proportional with the operation time (t) as expected.

The adsorption capacity of the adsorbent per unit external surface area of the adsorbent (q_a, kg adsorbate m^{-2}) is related to the capacity per unit mass (kg adsorbate kg^{-1} adsorbent) as follows by assuming spherical adsorbent particles:

$$\frac{q_s'}{q_a} = \frac{6}{\rho_{ads} D_p} \tag{10}$$

where, D_p is the particle size of the adsorbent (PWS).

Substitution of Eqn. (10) into Eqn. (9) yields the following equation,

$$t_b = \frac{q_a}{C_o Q}\frac{6}{\rho_{ads} D_p} m_{ads} - \frac{1}{KC_o}\mathrm{Ln}\left[\frac{C_o}{C_b} - 1\right] \tag{11}$$

A plot of experimental data in the form of break-through time (t_b) versus $6\, m_{ads}/(Q\, C_o\, \rho_{ads}\, D_p)$ results in a line with a slope of q_a and an intercept of $-(1/KC_o)$ Ln $(C_o/C_b - 1)$ for constant C_o and C_b values from which the adsorption capacity and the rate constant are determined.

MATERIALS AND METHODS

Experimental System

The experimental system consisted of a feed reservoir, a feed pump, and a completely mixed reactor placed on a magnetic stirrer. The adsorption reactor was made of plexiglass with a 15 cm diameter and a 30 cm height with a total volume of 5.3 litre. The feed reservoir contained the copper ion solution at pH = 5 to avoid copper ion precipitation which was fed to the reactor with a desired flow rate while the reactor contents containing the adsorbent (PWS) was mixed by a magnetic stirrer.

Experimental Procedure

Waste activated sludge samples from a paint industry wastewater treatment plant (DYO, Izmir, Turkey) was used after pre-treatment in fed-batch biosorption experiments since this sludge was found to be superior to the other sludges tested for biosorption of copper(II) ions (27). The sludge was dried, ground, and sieved to desired particle sizes to obtain the powdered waste sludge (PWS) samples. The PWS samples were pre-treated using five different pre-treatment solutions of 1% H_2SO_4, NaOH, NaOCl, Ethanol, and H_2O_2. A 200 ml of pre-treatment solution was mixed with 2 g of PWS in a 500 ml erlenmeyer flask and was placed on a gyratory shaker at 150 rpm and 25°C for 6 hours for pre-treatment. Pre-treated PWS was washed with deionized water on a filter paper until the filtrate pH was neutral. Pre-treatment with 1% H_2O_2 was found to be superior to the other methods yielding the highest biosorption capacity (27). Pre-treated and washed PWS samples were dried at 80°C, reground and sieved to different particle sizes between 53 and 231 μm.

The fed-batch operation was used to provide an alternative for adsorption column operations. In fed-batch operation, the feed copper ion solution was fed to a completely mixed tank containing the adsorbent (PWS) with a desired flow rate and no effluents were removed until the tank was full. The liquid volume in the tank increased linearly with time with a constant feed flow rate. The PWS in the tank was allowed to settle for an hour at the end of the operation and the clear supernatant was removed from the tank. The fed-batch operation was repeated with a new PWS solution. A control tank free of PWS was operated under the same conditions to determine the copper ion concentrations in the absence of the adsorbent. Difference between the Cu(II) ion concentrations in the control and the experimental tank was considered when calculating solid phase Cu(II) concentrations. The biosorbed Cu(II) ion concentrations in the adsorbent (solid) phase was determined by using the following equation.

$$q = \frac{V(C_c - C)}{m_{ads}} = \frac{(V_o + Qt)(C_c - C)}{m_{ads}} \tag{12}$$

where q is the biosorbed Cu(II) ion concentration in the solid phase (mg g^{-1}), V is the liquid volume in the adsorption tank which increased linearly with time (l), V_o is the initial volume in the ractor (11), t is the duration of the fed-batch experiment (10 h), C_c and C are the copper ion concentrations in the control and the adsorption reactors, respectively (mg l^{-1}), Q is the flow rate of the feed copper ion solution (0.25 l h^{-1}), and m_{ads} is the amount of adsorbent (PWS) in the adsorption reactor (2 g).

A set of experiments with six different particle sizes between 53 and 231 μm were performed while the feed Cu(II) concentration (200 mg l^{-1}), feed flow rate (0.25 l h^{-1}), and the mass of adsorbent (PWS, 2 g) was kept constant. Control experiments were performed under the same conditions of the adsorption experiments.

Experiments were started by placing 1 litre tap water and 2 g of PWS of desired particle size in the adsorption reactor. The pH in the feed and the reactor was adjusted to pH = 5 at the beginning which did not change much during the operation (pH = 5 ± 0.2). Copper(II) ion solution was fed to the reactor with a desired flow rate while the reactor contents were completely mixed by a magnetic stirrer. The operation was performed at a room temperature of 25 ± 2°C.

Analytical Methods

Samples (5 ml) were removed from the adsorption and the control reactor every hour which were centrifuged at 8000 rpm (7000 g) to remove solids before analysis. Clear supernatants after centrifugation were analyzed for Cu(II) ion concentrations using an Atomic Absorption Spectrometer (ATI Unicam 929 AA Spectrometer) at a wavelength of 324.8 nm.

RESULTS AND DISCUSSION

Effect of Particle Size on Copper Ion Biosorption

Six fed-batch biosorption experiments were carried out with six different particle sizes of PWS between 53 and 231 μm while the feed flow rate (0.25 l h^{-1}), feed Cu(II) ion concentration (200 mg l^{-1}) and the amount of PWS (2 g) were constant. A control tank was operated under the same conditions as the adsorption tank to determine the actual Cu(II) ion concentrations in the absence of adsorption. Percent copper ion removals in the experimental tank were based on the copper ion concentrations in the feed ($E = 1 - C/C_o$).

Figure 1 depicts break-through curves describing variations of copper ion concentrations in the adsorption reactor with time for different particle sizes of the adsorbent (PWS) in fed-batch experiments. Copper(II) ion concentrations increased with time due to increased occupation of binding sites on PWS

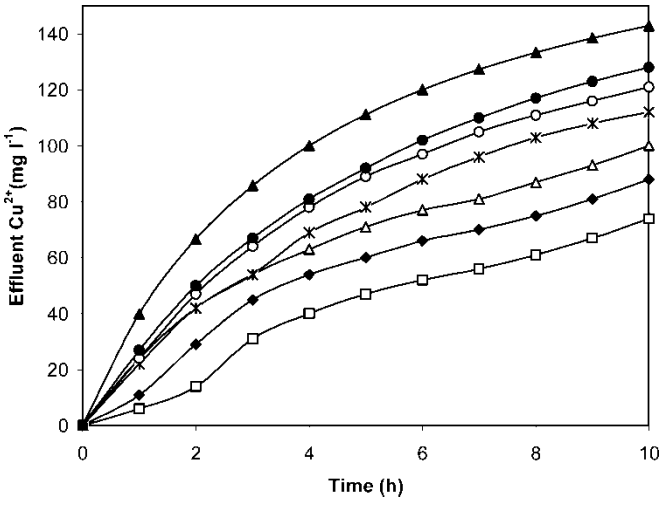

Figure 1. Break-through curves for copper(II) ion biosorption onto PWS with different particle sizes. D_p (μm): □ 53, ◆ 64, Δ 109, ∗146, ○ 163, ● 231, ▲ control.

surfaces for all PWS particle sizes. The aqueous phase contained much higher copper ions at high particle sizes due to limited surface area and therefore, limited binding sites on PWS surfaces. The final copper(II) ion concentration at the end of a 10 hours operation decreased from 128 mg l^{-1} to 74 mg l^{-1} when the average PWS particle size decreased from 231 to 53 μm. At large particle sizes ($D_p > 100$ μm) the extent of adsorption was limited by the surface area or the available binding sites on PWS surfaces. The reduction of particle size increased the extent of biosorption of Cu(II) ions significantly due to availability of a larger surface area of the PWS at small particle sizes. Break-through times (t_b) for different operations to obtain $C_b = 10$ mg l^{-1} in the effluent were read from the curves in Fig. 1 by drawing a horizontal line at $C_b = 10$ mg l^{-1} and reading the t_b values of the intersection points from the x-axis.

Variations of solid phase Cu(II) ion concentrations with time are depicted in Fig. 2 for different particle sizes of PWS in fed-batch experiments. Solid phase copper ion concentrations increased with time for all particle sizes due to continued binding of Cu(II) ions onto PWS surfaces. Biosorbed copper ion concentrations were higher at smaller particle sizes of PWS because of a larger surface area or binding sites on the PWS surfaces. The final biosorbed Cu(II) ion concentrations at the end of 10 hours of operation increased from 26 mg g^{-1} to 121 mg g^{-1} when the average particle size decreased from 231 to 53 μm. At large particle sizes the extent of biosorption was limited by the availability of the surface area or the binding sites on PWS surfaces yielding low solid phase (biosorbed) Cu(II) ion concentrations. Reduction in particle size of PWS increased the surface area of PWS and

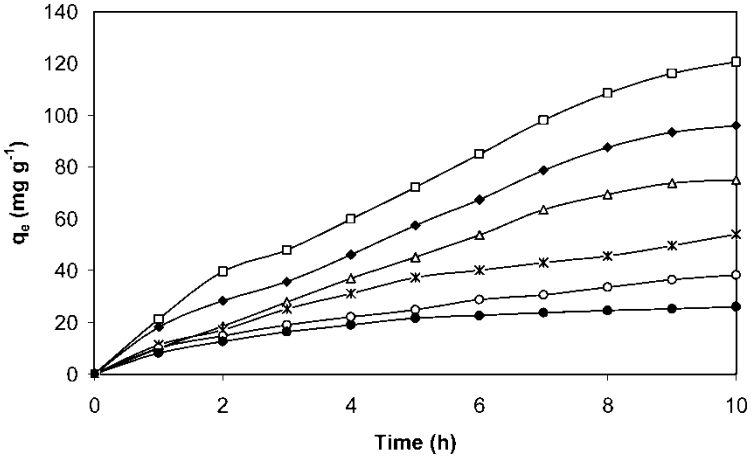

Figure 2. Variation of solid phase(biosorbed) Cu(II) ion concentrations with time for different particle sizes. D_p (μm): □ 53, ◆ 64, Δ 109, ∗ 146, ○ 163, ● 231.

resulted in higher biosorbed Cu(II) ion concentrations. The particle size of PWS should be lower than 53 μm in order to obtain high biosorbed Cu(II) ion concentrations.

Figure 3 depicts variations of effluent and solid phase(biosorbed) Cu(II) ion concentrations at the end of 10 hours of fed-batch operation with the particle size of PWS. Effluent Cu(II) ion concentration increased with increasing particle size due to lower surface area or binding sites on PWS at large

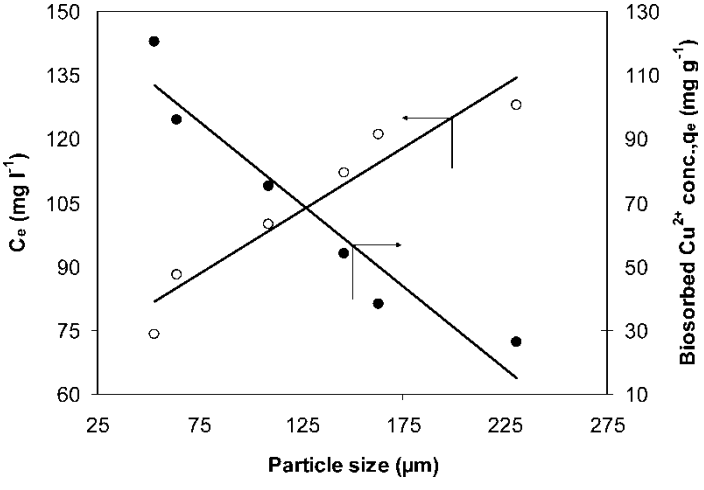

Figure 3. Variation of the effluent and the biosorbed (solid phase) Cu(II) ion concentrations with the particle size at the end of 10 hours of fed-batch operation.

particle sizes. In contrast to the effluent Cu(II) ion concentrations, the solid phase(biosorbed) Cu(II) ion concentrations decreased with increasing particle size because of a limited surface area or binding sites on PWS at large particle sizes. A decrease in particle size from 231 μm to 109 and further to 53 μm resulted in decreases in effluent Cu(II) concentrations from 128 mg l^{-1} to 100 and further to 74 mg l^{-1}, which yielded increases in biosorbed Cu(II) concentrations from 26 mg g^{-1} to 75 and further to 121 mg g^{-1}.

Variations of percent copper ion removals ($1 - C/C_o$) from the feed solution with the particle size are depicted in Fig. 4. The extent of copper ion removal decreased with increasing particle size or decreasing external surface area of the PWS. Percent copper ion removal decreased from 63% to 50 and further to 36% when the particle size increased from 53 μm to 109 and further to 231 μm. Again, this is because of the availability of a larger surface area or binding sites on PWS surfaces at small particle sizes.

Determination of Modified Bohart–Adams Equation Constants

Experimental data obtained at different particle sizes of the adsorbent in fed-batch experiments were used to determine the adsorption capacity of PWS and the rate constant for adsorption of Cu(II) ions onto PWS by using Eqn (11). Break-thtrough times (t_b) to obtain break-through Cu(II) concentration of 10 mg l^{-1} were determined using the data presented in Fig. 1. Break-through times were plotted against $6\,m/(QC_o\rho D_p)$ in Fig. 5 for different particle sizes ($\rho_{ads} = 1.2$ g $cm^{-3} = 1200$ kg m^{-3}). From the slope and

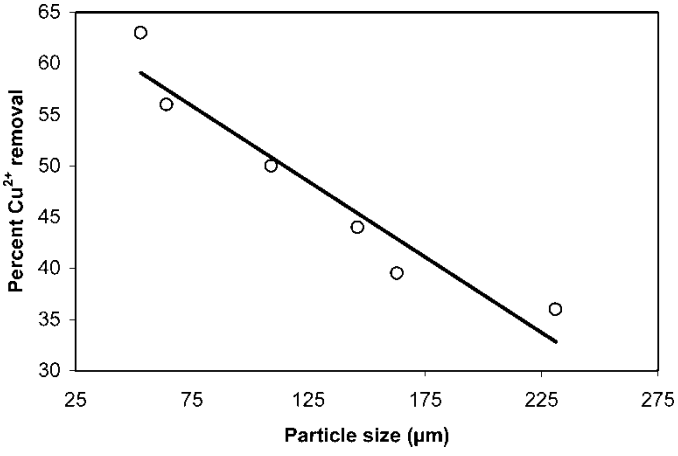

Figure 4. Variations of percent copper ion removals with the particle size of the adsorbent (PWS) at the end of 10 hours of fed-batch operation.

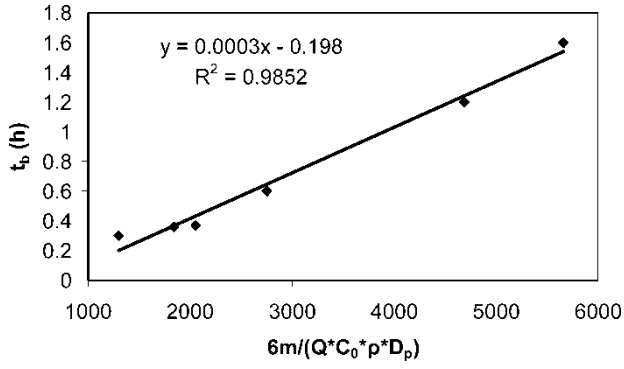

Figure 5. Break-through time versus $6\,m/(Q\ C_o \rho D_p)$ for determination of the constants of the modified Bohart-Adams equation.

the y-axis intercept of the line the following constants were obtained:

$$q_a = 0.0003\,\text{kg Cu m}^{-2}\,\text{PWS} = 0.3\,\text{g Cu m}^{-2}\,\text{PWS},$$
$$K = 74.35\,\text{m}^3\,\text{h}^{-1}\,\text{kg}^{-1}\ (R^2 = 0.985)$$

The surface area specified in the definition of q_a is the external surface area of spherical PWS particles excluding the pore surface areas.

The surface adsorption capacity, q_a ($\text{gCu} \cdot \text{m}^{-2}$) was converted to mass adsorption capacity, q_s' (gCu kg^{-1} PWS) by using Eqn. (10) for every particle size. The mass adsorption capacities of PWS were plotted against the particle size in Fig. 6. The mass adsorption capacities decreased with the increasing particle size because of a reduced surface area or binding sites on PWS surfaces at high particle sizes. An increase in particle size from 53 μm to 109 and further to 231 μm resulted in decreases in mass adsorption capacity of PWS from $28.3\,\text{mg g}^{-1}$ to 14 and further to $6.5\,\text{mg g}^{-1}$. Particle size of PWS should be lower than 53 μm in order to obtain high adsorption capacities for Cu(II) ions.

As compared to the literature studies the adsorption capacity of pretreated PWS for copper ions was superior to those obtained by using modified rice husk for copper and lead ion adsorptions in column operations (28). Also, the adsorption capacity of PWS was comparable with those reported in the literature for powdered activated carbon (25, 26). However, the adsorption rate constant obtained in this study ($K = 74.35\,\text{m}^3\,\text{h}^{-1}\,\text{kg}^{-1}$) was an order of magnitude higher than those obtained in PAC adsorption columns as reported in the literature ($K = 0.5\text{–}2\,\text{m}^3\,\text{h}^{-1}\,\text{kg}^{-1}$) (25, 26). This is because of elimination of mass transfer limitations encountered in adsorption columns by using a completely mixed adsorption reactor in fed-batch mode in our studies.

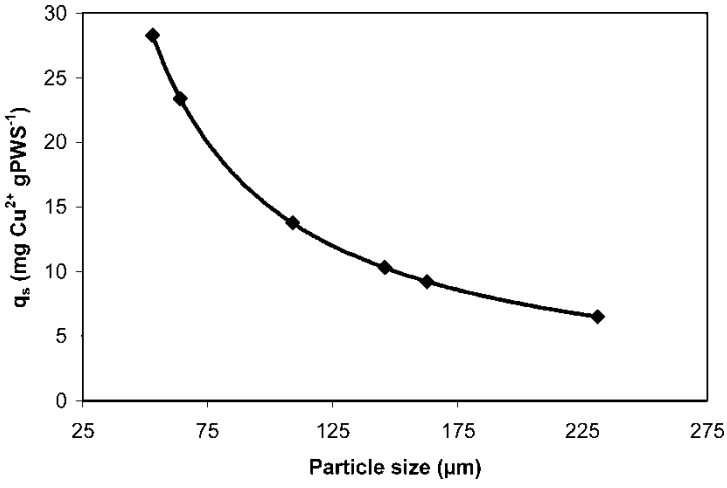

Figure 6. Variations of the mass biosorption capacity of the adsorbent (PWS) with the particle size.

CONCLUSIONS

A completely mixed tank operating in fed-batch mode was used for biosorption of Cu (II) ions onto pre-treated powdered waste sludge (PWS) instead of an adsorption column.

Fed-batch experiments were performed with different adsorbent (PWS) particle sizes between 53 and 231 μm at constant feed flow rate ($0.25\ l\ h^{-1}$), feed Cu(II) ion concentration ($200\ mg\ l^{-1}$) and the amount of PWS (2 g). Break-through curves were obtained for each particle size. Percent copper ion removal from the feed solution increased and the effluent Cu(II) ion concentrations decreased with decreasing particle size due to larger binding sites or external surface area of the PWS at small particle sizes. Biosorbed (solid phase) copper ion concentrations ($mg\ g^{-1}$) increased with decreasing particle size again due to availability of larger binding sites or surface area of the PWS at small particle sizes. A modifed Bohart-Adams equation was used to correlate the break-through time (t_b) with the particle size of the adsorbent. Experimental data obtained at different particle sizes were used to determine the constants of the modified Bohart-Adams equation. The surface and the mass adsorption capacities of the PWS were determined along with the adsorption rate constant. The mass adsorption capacity of PWS decreased with increasing particle size while the surface adsorption capacity was constant. The mass adsorption capacity of PWS was comparable with those obtained with the activated carbon in adsorption columns and superior to some of the other adsorbents reported in literature. The adsorption rate constant determined in our study

was an order of magnitude larger than those obtained in adsorption column studies using powdered activated carbon (PAC) due to elimination of mass transfer limitations encountered in adsorption columns. A completely mixed adsorption reactor operated in fed-batch mode was proven to be more advantageous as compared to the adsorption columns.

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