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Adsorption of Cu^{2+} by charcoal, waste biomass, *Pseudomonas putida* and *Penicillium* sp.

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Abstract

Wood charcoal and waste biomass collected from municipal waste-water-treatment plant, *Pseudomonas putida* and *Penicillium* sp. were used to remove Cu^{2+} from acidic waste water. The adsorption kinetics and the Cu^{2+} uptake capacity was found to be maximum in the case of *Pseudomonas putida*, and was affected by parameters such as pH, initial metal ion concentration, biomass amount and temperature. The adsorption phenomena obeyed Freundlich adsorption isotherm. Theoretical equilibrium concentrations calculated by using Freundlich adsorption isotherm were found to be in good agreement with the observed values. Theoretical number of stages required to reduce the Cu^{2+} concentration from the solution was predicted by using adsorption isotherm The rate-determining step was found to be diffusion controlled.

Keywords: Copper, diffusion controlled, adsorption isotherms, dual rate, rate-determining step, charcoal, waste biomass, *Pseudomonas putida* and *Penicillium* sp.

1. Introduction

Cu^{2+} is one of the most commonly encountered heavy metal pollutants in metallurgical waste water derived from electrical, electronic and brass industries. Conventional methods such as chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment and evaporation are usually not economically viable when the concentration of the metal ions is very small.[1, 2] Therefore, adsorption technology is being considered as an alternative method for the removal and recovery of heavy metal ions from natural and industrial waste water.[3, 4] Many biological and chemical adsorbents are known to be effective metal adsorbents. Microorganisms such as bacteria, fungi and algae have been extensively studied as a possible means to clean up Cu^{2+}-containing waste streams. Immobilized cells of *Pseudomonas putida* were reported[5] to adsorb Cu^{2+} from industrial effluents. Mycelial waste of *P. chrysogenum* collected from a penicillin-manufacturing plant was found to adsorb heavy metal ions like Cu.[6] The Cu^{2+}-adsorption characteristics of *Penicillium* sp. isolated from soil as well as Cu^{2+} uptake by *P. ochrochloran* were investigated.[7, 8] The biosorption of Cu^{2+} by activated sludge bacteria was investigated by Aksu *et al.*[9] Cu^{2+} uptake by fungi and activated sludge bacteria was studied and compared to select the most suitable biomass for the treatment of a metal-containing industrial waste waters.[10] Various chemical adsorbents like suspended solids in river water,[11] wood bark,[12] clay minerals,[13] activated carbon[14] and carbon black spheron '9'[15] have also been used to recover Cu^{2+} from waste streams.

The present paper describes the adsorption behavior of three different biomasses, (i) a bacteria (*Pseudomonas putida*, PP), (ii) a fungus (*Penicillium* sp., PS) and (iii) a mixed culture (waste biomass, WB) and the adsorption behavior is compared to a chemical adsorbent (wood charcoal, WC). In addition, an evaluation of the kinetics of adsorption is presented to evaluate the rate-determining step in each case.

2. Experimental

2.1. *Adsorbents*

The WC sample contained 25% volatile matter, 11.6% ash, 9.8% moisture and 47% fixed carbon. The sample was crushed, sieved and used for adsorption studies. The WB sample was collected from the Bhubaneswar Municipality waste-water-treatment plant. The sample was sterilized by autoclaving and later dried. WB contained both Gram-positive and -negative microorganisms. The metal contents were Mn–0.0556%, Fe–1.58%, Zn–0.022%, Cu–0.0035%, Ni–0.0025% and Co–0.00175%.

PP and PS samples were collected from the Maharashtra Association for the Cultivation of Science, Pune, India. The species were grown in the media using sucrose as the main carbon source. The media used, respectively, were

For PS: (g/dm^3) NH_4NO_3–3.0, KH_2PO_4–1.0, $MgSO_4$, $7H_2O$–0.5 and Sucrose–50.0.
For PP: (g/dm^3) $(NH_4)_2SO_4$–0.25, $MgSO_4,7H_2O$–0.75, $Na_2HPO_4,12H_2O$–0.3, KH_2PO_4–0.25, Yeast extract–1.0 and Sucrose–20.0.

Cultures were grown for 72 hours and sterilized and the biomass was harvested by centrifugation. The product was washed thoroughly, dried, ground and used for adsorption studies.

2.2. *Adsorbates*

A stock solution of copper was prepared by dissolving the required amount of AR $CuSO_4$, $5H_2O$ in distilled water.

2.3. *Adsorption isotherm studies*

Adsorption measurements were made in a glass reactor. The samples were stirred mechanically at different temperatures controlled by a thermostat to ±0.5°C. The pH of the solution was adjusted with H_2SO_4 or diluted NaOH. Samples were taken at regular time intervals and an equal amount of original solution was added to maintain the volume constant. Unless specified the adsorption experiments were conducted as follows: Time–for PS, PP and WB, 60 min and for WC, 150 min, pH–6.0, Temperature–30°C, Solution volume–for WC, PP and WB, 0.2 dm^3 and for PS, 0.8 dm^3. Cu^{+2} concentration in experiments using WC was 1,000 mg/dm^3 and for PP, PS and WB 20 mg/dm.^{3} Weight/volume (%) was between 0.05% and 10.0% in all experiments and for all experimental conditions.

2.4. *Analyses*

Cu analyses were made by using a Perkin Elmer-3100 atomic absorption spectrophotometer.

3. Results and discussion

3.1. *Effect of time*

Adsorption studies were carried out for more than 4 hours. In all the cases, the adsorption kinetics can be subdivided into two sections, i.e. an initially faster reaction followed by a slower reaction (Fig. 1). The fast initial rate may be due to the abundant availability of chelating agents present on the surface of the adsorbents but we are yet to understand the subsequent slow reaction.

A similar adsorption pattern was reported by several authors.[16, 17] The initial rates of adsorption for PP, WB, PS and WC can be calculated to be 3.0, 0.31, 0.21 and 1.76 mg g^{-1} min^{-1}, respectively, hence, PP > WC > WB > PS.

3.2. *Effect of pH*

To evaluate the effect of pH on Cu^{2+} adsorption, the pH was varied between 2.0 and 6.5. The adsorption of Cu increased from pH to pH and had little effect beyond 4.0. More specifically, PP and WB showed hardly any improvement and was unchanged for WC and PS beyond 3.0 and 5.0, respectively (Fig. 2).

In order to explain the pH effect, the chemistry of the adsorbent surface as well as that of the metal ion has to be understood. The main species formed during the hydrolysis of Cu^{2+} in this pH range are the hydroxyl-bridged polynuclear species $Cu_n(OH)_{2n-2}^{2+}$ and not $Cu(OH)^+$.[18] Since dead biomass was used in these studies, the metal accumulation is due only to surface interactions.[19] Charcoal consists of many organic compounds[20] and the cell wall of biomass consists of various biopolymers like chitin, amino acids, lipids and polysaccharides.[21] These

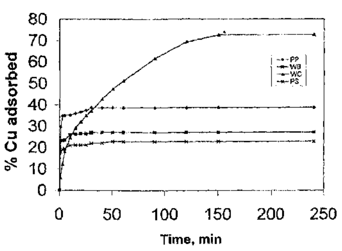

FIG. 1. The adsorption behavior of different adsorbents as a function of time.
Conditions: pH–2.6, 3.3, 4.0 and 4.4 for WC, WB, PS and PP, respectively, temperature–30°C, solution volume–0.2 dm^3 for WC, PP and WB, and 0.8 dm^3 for PS. Cu^{2+} concentration for WC is 1000 mg/dm^3 and for PP, PS and WB 20 mg/dm^3, %(w/v) – 0.05, 0.5, 0.0625 and 10 for PP, WB, PS and WC, respectively.

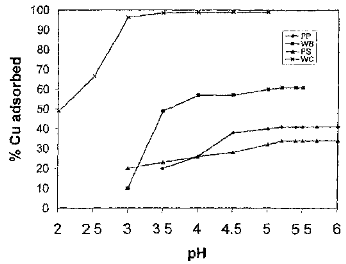

FIG. 2. Variation of percentage of adsorption with change in pH for all the adsorbents.
Conditions: Time–for PS, PP and WB 60 min and for WC 150 min, temperature–30°C, solution volume–0.2 dm^3 for WC, PP and WB and 0.8 dm^3 for PS, Cu^{2+} concentration for WC is 1000 mg/dm^3 and for PP, PS and WB 20 mg/dm^3, %(w/v)–0.05, 0.5, 0.0625 and 10 for PP, WB, PS and WC, respectively.

functional groups are generally negatively charged and therefore the adsorption of Cu^{2+} on the adsorbent surface would be due to electrostatic attraction between negatively charged surface of the biomass and positively charged $Cu_n(OH)^{2+}_{2n-2}$. This type of attraction is maximum at a pH when the cation is hydrolyzed. At low pH, part of the organic compounds present on the WC surface and in the cell wall of the bioadsorbents is hydrolyzed[22] or protonated thereby reducing the amount of adsorbing sites on the surface of the adsorbents for Cu^{2+}. Therefore, at low pH, the percentage of Cu^{2+} adsorption decreases.

3.3. *Effect of temperature*

The effect of temperature between 30°C and 70°C was studied (Fig. 3). In the case of PS and WC, the adsorption increased up to 40°C and 50°C, respectively, and showed negative effect beyond these values. The negative effect may be due to higher degree of hydrolysis of chitin and other chelating compounds at higher temperature.[23] In the case of PP and WB, there is no remarkable change in the percentage of adsorption (Fig. 3). The apparent activation energies in each case were calculated by using the Arrhenius equation and were found to be 11.87, 10.5, 10.04 and 13.64 kJ/mole, respectively, for WC, PP, WB and PS.

3.4. *Effect of initial metal ion concentration*

At constant contact time (150 min for WC and 60 min for WB, PP and PS) and pH (3.0, 4.0, 4.5 and 5.0, respectively), the adsorption studies were carried out by varying the Cu^{2+} concentration. It was observed that the adsorption kinetics as well as loading capacity increased with increase in metal ion concentration, whereas percentage of adsorption showed a reverse trend. This may be due to higher probability of collision between metal ions and adsorbent surfaces.

The relationship between the amount adsorbed and the concentration of the solution can be expressed by a mathematical equation known as Freundlich adsorption isotherm[24]

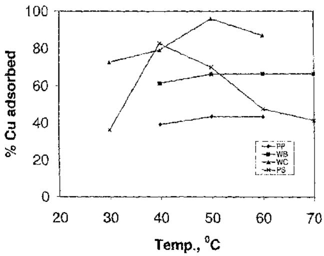

FIG. 3. The effect of temperature on adsorption for all the adsorbents.
Conditions: Time for PS, PP and WB is 60 min and for WC 150 min, pH is 5.0, solution volume for WC, PP and WB is 0.2 dm^3 and for PS 0.8 dm^3, Cu^{2+} concentration for WC is 3000 mg/dm^3 and for PP, PS and WB 20 mg/dm^3, %(w/v)–0.05, 0.5, 0.0625 and 10 for PP, WB, PS and WC, respectively.

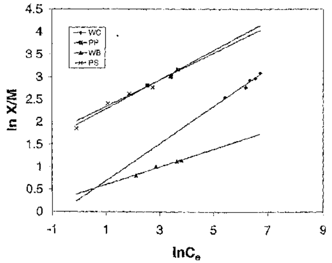

FIG. 4. Plot of ln X/M vs lnC_e for all the four adsorbents studied with different initial Cu^{2+} concentrations of the solution.
Conditions: Time for PS, PP and WB 60 min and for WC 150 min, PH is 5.0, solution volume for WC, PP and WB is 0.2 dm^3 and for PS 0.8 dm^3, temperature–30°C, %(w/v)–0.05, 0.5, 0.0625 and 10 for PP, WB, PS and WC, respectively.

$$X/M = KC_e^{1/n} \tag{1}$$

where X is the amount of Cu^{2+} adsorbed, mg $= (C_I - C_F)V$, C_I the initial concentration of the solution, mg/dm^3, C_F the final concentration of the solution, mg/dm^3, V the volume of the solution, dm^3, M the mass of biomass, g, K, n are Freundlich constants, C_e the equilibrium Cu^{2+} concentration, mg/dm^3, and n and K values can be obtained from the slope and intercept of a graph if ln X/M is plotted against ln C_e (Fig. 4).

3.5. *Effect of pulp density*

The amount of adsorbent was varied from 0.1 to 1 g keeping constant other parameters like pH (5.0), temperature (30°C), Cu^{2+} concentration (20 mg/dm^3) and solution volume (0.2 dm^3) to ascertain the loading capacity of Cu. It was observed that an increase or decrease in the adsorbent quantity strongly affected the quantities of Cu^{2+} removed from the solution. The loading capacity increased with decrease in adsorbent.

In order to find out the theoretical number of stages required to remove Cu^{2+} from a solution of 16 mg/dm^3 in a continuous run, the experiments were carried out in a batch scale by varying V_0/X_0 ratio (V_0 the initial solution volume, dm^3, and X_0 the adsorbent amount, g) with the same parameters. An equilibrium curve was obtained by plotting a graph between equilibrium concentration, C_e, and loading (mg metal adsorbed per gram of adsorbent). An operation line having slope $V_0/X_0 = 1$ was drawn from which it was observed that in two stages the Cu^{2+} ion concentration can be reduced from 16 mg/dm^3 to 2.5, 4.3, 8.6 and 11.8 mg/dm^3 for PP, WC, WB and PS, respectively (Fig. 5). Therefore, based on the results, a multistage reactor can be designed depending on the V_0/X_0 ratio in order to treat the actual waste water.

3.6. *Effect of mechanical agitation*

Under optimized conditions of temperature and pH, the adsorption studies were carried out by varying the rate of mechanical agitation. It was observed that in all cases, the adsorption of Cu^{2+} increased up to 300 rpm and beyond it no further increase was observed. From this observation it is concluded that the reaction is diffusion controlled in nature.

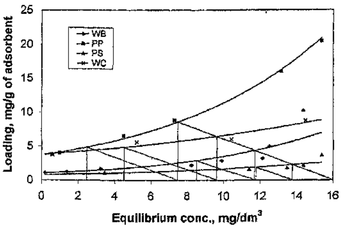

FIG. 5. Cu^{2+} adsorption isotherm for all the four adsorbents studied under identical conditions, i.e. pH–5.0, temperature–30°C, Cu^{2+} concentration–20 mg/dm^3 and solution volume–0.2 dm^3.

3.7. *Mechanism of adsorption*

In an adsorption reaction, the adsorbate must come in contact with the adsorbent, so that a part of the adsorbate would be adsorbed on the adsorbent surface. Simultaneously, a part of the adsorbed material would be desorbed. Therefore, the bulk Cu^{2+} concentration can be expressed[16, 25–29] as:

$$C = D \exp(-K_0 t) + C_e \tag{2}$$

where C is bulk concentration, mg/dm^3, D the fitting parameter, K_0 the constant $= k_0 M$, k, the mass-transfer adsorption coefficient, C_e the equilibrium Cu^{2+} concentration, and t the time in min.

Therefore, K_0 and D can be calculated graphically from the slope and intercept, respectively, if $\ln(C\text{-}C_e)$ is plotted against t. Table I shows the values of K_0 and D along with coefficients of determination of some of the experiments. From the coefficients of determination, it can be concluded that eqn (2) is adequate to calculate mass-transfer coefficients of various adsorption experiments. Therefore, using K_0 and D values, obtained from the graph and C_e values, the rate of adsorption can be predicted.

3.8. *Rate-determining step*

In the adsorption kinetics, the metal ion from the bulk solution should travel to the thin liquid film surrounding the adsorbent surface. In this situation, there are two alternatives, i.e. the thin liquid film may produce a diffusion barrier for the metal ion to penetrate through or the diffusion barrier may be negligible. The former is known as film diffusion and the latter as adsorption controlled.

3.9. *Film diffusion controlled*

In the film diffusion-controlled process, the bulk concentration, C, would be at a higher concentration than the interfacial concentration, C_s, i.e. $C > C_s$. Therefore, k_0 can be written[16,28,29] as

$$k_0 = K_m S C_0 M/(C_0 - C_e) \tag{3}$$

where C_0 is the initial Cu^{2+} concentration, mg/dm^3, M the mass of adsorbent, g, and K_m the mass-transfer coefficient between the bulk liquid and the adsorbent particles.

K_m value was reported[30] to depend on the particle size of the adsorbate, rate of energy dissipation per unit mass of fluid and the kinematic viscosity of the solution. Therefore, for the same temperature and agitation speed, the K_m value would be constant. Presuming specific surface area (S) of a particular adsorbent to be constant, if the rate-determining step is film diffusion, then $K_m S$ should be constant for different experimental conditions. Table I shows the $K_m S$ values for different experiments which are almost constant at constant temperature and pH. Therefore, it can be concluded that the rate-determining step is film diffusion which is also evident from the effect of agitation speed.

3.10. *Adsorption rate controlled*

In the case of adsorption rate-controlled process, the bulk concentration, C, and the interfacial concentration, C_s would be the same, because the film layer around the adsorbent

Table I
Calculated values of D, K_o and K_mS along with the adsorption conditions

PH	Temp. (^oC)	Initial metal ion concentration (mg/dm^3)	Pulp density %(w/v)	LnD (mg/dm^3)	K_0 (min^{-1})	R^2	K_mSX10^3 (dm^3.g^{-1}.min^{-1})
Charcoal							
5.2	30	2087	10	7.18	0.02	0.97	0.87
5.2	30	2637	10	7.35	0.02	0.98	0.85
5.2	30	3031	10	7.52	0.02	0.98	0.84
5.2	30	2087	5	6.47	0.02	0.97	0.88
Pseudomonas putida							
5.4	40	21	0.25	1.85	0.3	0.98	500.0
5.4	40	41	0.05	1.75	0.2	0.84	550.0
5.4	40	20	0.10	1.5	0.4	0.89	510.0
5.4	40	30	0.05	1.8	0.1	0.88	523.0
Waste biomass							
5.7	30	31	0.5	1.54	0.11	0.98	0.48
5.7	30	44	0.5	1.75	0.13	0.93	0.47
5.7	30	61	0.5	2.35	0.19	0.96	0.48
5.7	30	20	0.5	1.9	0.19	0.92	0.46
Penicillium sp.							
6.5	30	21	0.0625	0.96	0.031	0.88	22.0
6.5	30	4.9	0.0625	0.12	0.03	0.87	27.0
6.5	30	9.9	0.15	0.59	0.02	0.94	24.0
6.5	30	9.8	0.3	0.67	0.04	0.89	29.0

R^2 = coefficients of determination

particle may be so thin that it may not play any major role. Therefore, $C = C_s$ and K_0 can be written as[16, 28, 29, 31]

$$K_0 = K_d C_0 / C_e \tag{4}$$

where $K_0 = k_0 M$.

K_0 in eqn (4) is independent of the adsorbate concentration. The desorption rate constant, K_d, can be calculated from eqn (4). Table II shows the K_d values for different amounts of adsorbent used, keeping the pH and temperature constant. From Table II, it can be concluded that the adsorption may not be rate controlling as the K_d values were observed to decrease with increase in the amount of adsorbents for adsorption studies.

4. Conclusions

From detailed adsorption studies, PP was found to be the best biomass in terms of adsorption kinetics, whereas PS was found to be suitable in terms of Cu^{2+} uptake. The adsorption rate showed dual rate, i.e. initial faster followed by slower rate and the adsorption kinetics increased with increase in pH, biomass as well as initial metal ion concentration in all the cases. With increase in temperature, the kinetics increased up to a certain temperature, there-

Table 2
Calculated K_d values

Amount of adsorbent (g)	C_e/C_0	K_0 (min^{-1})	K_d (min^{-1})
Charcoal			
20	0.139	0.023	3.2×10^{-3}
40	0.00018	0.05	0.88×10^{-3}
Pseudomonas putida			
0.05	0.659	0.044	28.98×10^{-3}
0.5	0.175	0.082	14.3×10^{-3}
Waste biomass			
0.1	0.723	0.194	14.0×10^{-3}
0.3	0.617	0.08	4.9×10^{-3}
Penicillium sp			
0.1	0.48	0.08	38.4×10^{-3}
1.0	0.19	0.03	5.7×10^{-3}

after WC and PS showed a reverse trend, while PP and WB showed no remarkable change. The loading capacity increased with decrease in biomass amount as well as increase of initial Cu^{2+} concentration. An equilibrium isotherm has also been developed for each of the adsorbents studied in order to predict the number of stages required to reduce the Cu^{2+} concentration in a continuous operation. The adsorption process followed the Freundlich adsorption isotherm and the equilibrium concentrations for different experiments were calculated by using this isotherm. A mathematical correlation was made between mass-transfer adsorption coefficient (K_0), equilibrium Cu^{2+} concentration (C_e) and the bulk Cu^{2+} concentration (C_0) for different times (t). The rate-determining step was found to be diffusion controlled rather than adsorption controlled. The adsorption results were well explained by using mass-transfer adsorption model.

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