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Adsorption and toxicity of heavy metals on activated sludge

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ABSTRACT: The adsorption of Cu, Cd, Ni, Zn, and Cr from synthetic solutions on powdered activated carbon (PAC), activated sludge, and dried sludge were investigated under laboratory conditions to assess its ability to remove heavy metals. The adsorption efficiency increased rapidly within the first 30 min and then slowed down as it approached a steady state after 5 h of contact time. The results showed that activated sludge and PAC had a higher adsorption capacity than dried sludge. However, PAC showed a better adsorption capacity for Cu, Zn, and Ni than activated sludge. The maximum adsorption capacity, as quantified by the Langmuir parameter Q for activated sludge was 44, 30, 24, 23, and 18 mg/g for Cu, Ni, Cd, Cr, and Zn, respectively. In the case of dried sludge, the respective values of Q were 20, 13, 11, 3, and 10 mg/g. The acute toxicity of these five heavy metals to the activated sludge microorganisms was determined on the basis of the reduction in the specific oxygen uptake rate (SOUR). The results obtained from the SOUR measurements indicated a decreasing toxicity scale, Cu $>$ Cd $>$ Ni $\simeq$ Cr $>$ Zn on activated sludge microorganisms.

KEYWORDS: acute toxicity, adsorption capacity, biomass, isotherms, specific oxygen uptake rate

INTRODUCTION

Copper, zinc, nickel, cobalt, silver, cadmium, and chromium are extensively used in electroplating and metal-processing industries. Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora, and fauna, which in turn, may enter into the human food chain and result in health problems[1,2]. To mitigate the heavy metal pollution, many processes like adsorption, precipitation, coagulation, ion exchange, electro-dialysis, electro-winning, electro-coagulation, and reverse osmosis have been developed[3–6].

The presence of heavy metals in wastewater is of interest because of their known toxic effects on the receiving environment and also on the performance of biological waste treatment processes[7,8]. The toxicity of Hg, Ni, and Cd shock loads of around 20 mg/l on activated sludge have been shown to depend on the metal (with Hg being the most toxic), the sludge age, and the specific metal adsorption site on the microbial flocs[9].

Extracellular polymeric substances (EPS) are reported to be actively involved in the biosorption of metals by activated sludge. EPS, which are secreted in part by microorganisms during growth, consist of various organic substances such as polysaccharides, uronic acids, proteins, nucleic acids, and lipids. It has been suggested that the mechanism of sorption is based on exchange reactions, complexation with negatively charged groups, adsorption, and precipitation[10–12]. Exposure to heavy metals has however been reported to cause a change in the composition (monitored through biomass C/P ratio) of extracellular polymeric substances[13].

Among the numerous methods to measure metal toxicity, the most widely used are enzymatic and nitrification inhibition, effluent turbidity, and oxygen uptake rate[14–16]. It has been difficult to compare results obtained with the different methods. For example, the following sequences of heavy metal toxicity on bacterial communities in activated sludge have been reported[17,18]: Cd $>$ Cu $>$ Zn $>$ Cr $>$ Pb, Cd $>$ Cr $>$ Cu $>$ Pb $>$ Zn. This discrepancy between the two studies resulted from both the type and structure of the bacterial community.

The aim of present study is to investigate the capacity of activated sludge and dried sludge to adsorb the heavy metals Cu(II), Cd(II), Ni(II), Zn(II), and Cr(III). The toxic effects of heavy metals on the activity of microbes through specific oxygen uptake rate (SOUR) measurements was also examined. The ability of powdered activated carbon and dried sludge to reduce the toxic effects of heavy metals on activated

sludge microorganisms was also studied. The results provide a useful insight into the metal uptake by activated sludge and highlight the operating parameters controlling metal toxicity.

MATERIALS AND METHODS

Activated sludge system

A sequencing batch reactor (SBR) was used to provide activated sludge for heavy metal uptake and specific oxygen uptake rate (SOUR) studies. The SBR was operated in a cycle time of 6 h. Each cycle consisted of 5 phases: fill (0.5 h), react (3.5 h), settle (1.0 h), draw (0.75 h), and idle (0.25 h). The activated sludge seed was obtained from a municipal wastewater treatment plant that received no industrial wastewater and was acclimatized in the laboratory by feeding it with a synthetic wastewater consisting of a base mix of 188 mg/l bacto-peptone, 563 mg/l sucrose, and nutrients and buffer solution (344 mg/l NH_4Cl, 49 mg/l $MgSO_4$, 11.3 mg/l $FeCl_3$, 250 mg/l KH_2PO_4). When activated sludge was acclimatized to the synthetic wastewater, it was used for adsorption and SOUR studies. During the steady state, the sludge age, mixed liquor suspended solids (MLSS), SVI, and SOUR in the SBR system were around 6 days, 4500 mg/l, 85 ml/g, and 65 mg O_2/g MLSS.h, respectively.

Adsorption study

This study was conducted to determine the capacity of powdered activated carbon (PAC), activated sludge, and dried sludge for Cu(II), Cd(II), Zn(II), Ni(II), and Cr(III) adsorption. A known amount of adsorbant was shaken with 100 ml of heavy metal solutions of various concentrations (10–100 mg/l), for a contact time of 5 h. The solutions were filtered and the supernatants were analysed for heavy metal residues using ICPS-7000 (Shimadzu). The adsorption efficiency was calculated by dividing the removed heavy metal by the initial heavy metal concentration. The activated sludge used in this study was collected from the SBR reactor during the idle phase. The dried sludge in this study was prepared by drying the wastage sludge from the SBR reactor in an oven. The activated sludge was washed with tap water and distilled water, filtered, and then dried in an oven at 105 °C. The dried sludge was then ready for the adsorption study.

Isotherm model

The equilibrium between an adsorbate immobilized on an adsorbant and the adsorbate remaining in the aqueous phase is usually presented by adsorption isotherms. The data obtained from adsorption of heavy metals were modelled using Freundlich and Langmuir isotherms. The linear form of the Langmuir and Freundlich isotherms are given, respectively, by

$$\frac{C}{q} = \frac{1}{bQ} + \frac{C}{Q},$$

$$\log q = \log K + \frac{1}{n}\log C,$$

where q is the amount of metal adsorbed per gram of sorbent (mg/g), C the equilibrium concentration of the adsorbate (mg/l) and Q and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. K and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Specific oxygen uptake rate (SOUR) determination

The inhibitory effects of Cu(II), Cd(II), Zn(II), Ni(II), and Cr(III) on the microorganisms activity in an activated sludge were studied by monitoring the change of SOUR. A sample of 50 ml mixed liquor was collected from the SBR reactor and placed in a BOD bottle which was subsequently filled with a fully aerated heavy metal-containing base solution. The concentrations of heavy metal tested were varied from 0 to 50 mg/l. The dissolved oxygen (DO) concentration was measured with a DO meter (TOA Electronics Ltd) at 30 s interval until the DO was completely exhausted. To study the effect of adsorbant on the activity of the activated sludge microorganism, powdered activated carbon (PAC) and dried sludge with concentrations varying from 0 to 4000 mg/l were added into the BOD bottle, which was filled with a fully aerated 35 mg/l heavy metal-containing base solution. The sample was filtered to determine the MLSS concentration.

The SOUR is the OUR per unit of dry biomass and is given by [16]

$$\text{SOUR} = -60\,G/X \quad (\text{mg O}_2\text{/g MLSS.h}), \qquad (1)$$

where G is the slope of the linear portion of the DO decline curve in $\text{mg l}^{-1}\text{min}^{-1}$, and X is the MLSS concentration in g/l.

RESULTS AND DISCUSSION

Effect of contact time on adsorption efficiency

The uptake rates of Cu, Cd, Zn, Ni, and Cr are shown in Fig. 1. The adsorption efficiency increased rapidly within the first 30 min and then slowed, approaching a steady state after 5 h. After this equilibrium period, the amount of adsorbed metal ions did not change

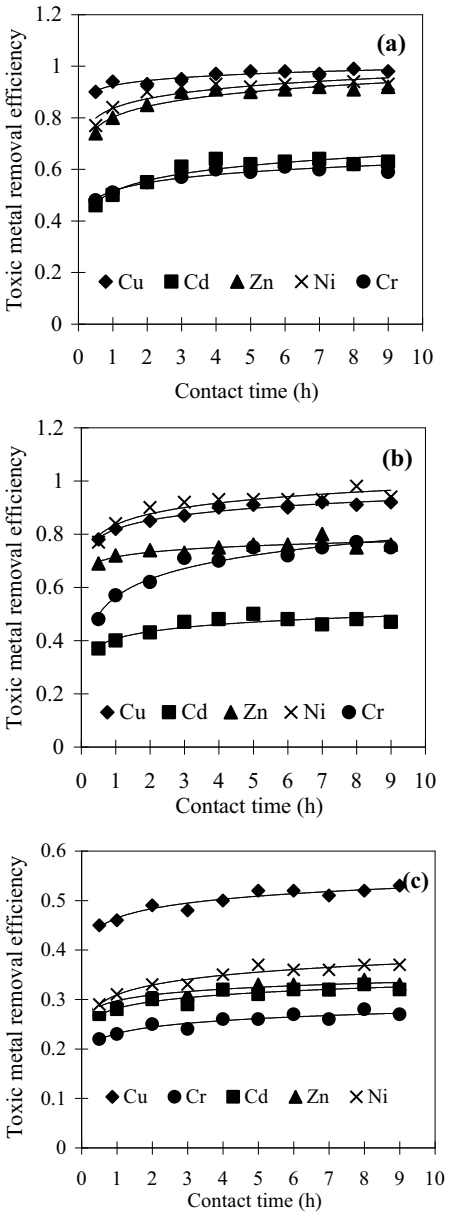

Fig. 1 Effect of contact time on adsorption efficiency of the toxic metals on (a) PAC, (b) activated sludge and (c) dried sludge.

significantly with time. As a result, the equilibration time was set to 5 h for subsequent experiments.

The adsorption profile of Cu, Cd, Zn, Ni, and Cr by activated sludge indicates that adsorption occurs in two stages: a rapid surface binding followed by a slow intracellular diffusion[19–21]. Dried sludge, which is non-living biomass, is generally used for adsorption studies because it eliminates the problem of heavy metal toxicity. As with the adsorption profile of metals by activated sludge, the adsorption efficiency of metals by dried sludge was rapid in the first phase and was followed by a slow phase. The determination of contact time as well as adsorption efficiency is important in selecting a retention time period suitable to achieve optimum operation in a biological reactor[20]. Generally, the results obtained show that the activated sludge and dried sludge could be used as bio-adsorbants in removing heavy metals from wastewater. In a real wastewater treatment plant, the heavy metals are usually removed by pH adjustment followed by coagulation and flocculation processes. The PAC also can be packed in a column to treat wastewater containing small amounts of heavy metals. Since PAC is expensive, activated sludge is proposed as a cheaper alternative. In fact, biological wastewater systems are mainly designed to remove organic matter and the side-benefits can be observed in the treatment of heavy-metal-bearing streams[7,16]. In a biological treatment process, the activated sludge from the final clarifier must be returned to the aeration tank depending on the desired mixed liquor, suspended solids, or sludge age. The excess activated sludge is always thickened, dried, and then disposed by landfill. Thus the reuse of this waste is needed for the process to be economical.

Adsorption isotherm

When C/q was plotted against C, straight lines with a slope of $1/Q$ were obtained (Fig. 2). This showed that the adsorption of Cu, Cd, Zn, Ni, and Cr followed the Langmuir isotherm. However, the plot of $\log q$ against $\log C$ showed that the adsorption did not fit well to the Freundlich model. The Langmuir constants (b and Q) and Freundlich constants (K and $1/n$) were calculated and the values are given in Table 1. The regression correlation coefficients for all the metal adsorbants are very high according to their Langmuir isotherms.

The adsorption capacity, Q, indicates that the uptake of Cu, Cd, Zn, Ni, and Cr by PAC and activated sludge was higher than that of the dried sludge. However, PAC showed a better adsorption capacity for Cu, Zn, and Ni than activated sludge. According to the Langmuir parameters, the maximum adsorption capacity for activated sludge in this study followed the order of Cu $>$ Ni $>$ Cd $>$ Cr $>$ Zn. Chua et al[22] have reported that metals adsorbed by activated sludge follow an adsorption capacity sequence of Cu $>$ Cr $>$ Zn $>$ Pb. Luo et al[23] also reported the same trend (Cu $>$ Cd $>$ Zn) using waste activated sludge. Both studies showed that the adsorption capacity of the sludge for Cu is the highest among the three ions. Our results also demonstrated that activated sludge

Table 1 Isotherm model constants for adsorption of heavy metals on PAC, activated sludge, and dried sludge.

		Langmuir			Freundlich		
Adsorbant	Adsorbate	Q (mg/g)	b (l/mg)	R^2	K	$1/n$	R^2
PAC	Cu	61	0.430	0.995	30.28	0.17	0.978
	Cd	22	0.195	0.991	12.76	0.11	0.834
	Zn	29	1.008	0.992	21.30	0.06	0.935
	Ni	33	0.384	0.998	24.54	0.06	0.783
	Cr	10	0.105	0.940	NA	NA	NA
Activated Sludge	Cu	44	0.278	0.994	22.14	0.15	0.986
	Cd	24	0.083	0.958	8.49	0.21	0.906
	Zn	18	0.337	0.996	10.97	0.11	0.861
	Ni	30	0.093	0.981	9.12	0.24	0.981
	Cr	23	0.119	0.949	12.22	0.12	0.635
Dried Sludge	Cu	20	0.192	0.996	8.84	0.18	0.965
	Cd	11	0.047	0.964	2.28	0.31	0.924
	Zn	10	0.204	0.994	5.73	0.11	0.848
	Ni	13	0.067	0.949	4.02	0.22	0.894
	Cr	3	0.241	0.972	1.43	0.15	0.847

adsorbed copper to a larger extent than other metal ions.

In the case of the dried sludge, the value of Q appears to be substantially higher for the copper adsorption (20 mg/g). Langmuir parameters for dried sludge in heavy metal adsorption also indicated a maximum adsorption capacity of 13 mg/g for nickel, 11 mg/g for cadmium, 10 mg/g for zinc, and 3 mg/g in chromium. This result is similar to that reported by Lister and Line[24]; the adsorption capacity trend they obtained is in the order Cu $>$ Ni $>$ Cd $>$ Zn $>$ Cr.

Effects of heavy metals on activated sludge microorganisms

Generally, increasing the heavy metal concentrations resulted in a corresponding reduction in the oxygen uptake rate by activated sludge microorganism (Fig. 3). The addition of heavy metals inhibited the activities of microorganisms in biodegradation processes. Subsequently the oxygen uptake by microorganisms to degrade the substrates was decreased. The results obtained from the SOUR measurements indicate a decreasing toxicity scale, Cu $>$ Cd $>$ Ni $\simeq$ Cr $>$ Zn, which is in partial contrast to those shown by the adsorption isotherm (Cu $>$ Ni $>$ Cd $\simeq$ Cr $>$ Zn). Our investigation showed that the Cu is the most adsorbed and toxic to activated sludge microorganisms. These results agree with Ref. 20 where the effects of Cr, Cu and Zn on the performance of sequencing batch reactor systems such as TOC, SS, and MLSS were examined. From the data, Cd is less adsorbed but more toxic than Ni. The reversal of Ni and Cd in the adsorption and toxicity trends could probably be explained by the age of the sludge. The sludge age exerts a selective action on Ni uptake and toxicity. As the sludge age increased, Ni uptake also will be increased and the metal toxicity will be decreased. However, sludge age influences only Cd uptake and not toxicity. The Cd affinity decreases with increasing sludge age. Therefore this indicates different sludge adsorption sites for the metals employed. Cd is adsorbed on extracellular polymer slimes and Ni on capsular polymers and the cellular wall[9]. The high adsorption capacity demonstrated by the activated sludge can be attributed to the presence of EPS. Many authors have shown that EPS production is enhanced in the presence of toxic compounds, and that because EPS exhibit chelating properties they could be involved in toxicity mitigation[25,26]. EPS in activated sludge flocs protect the bacterial community against chemicals that establish interactions with the polymer matrix by impeding access of the chemical to the bacterial cells[27].

Effects of adsorbants on activated sludge microorganisms

The addition of PAC and dried sludge to the base solution increased the SOUR by activated sludge microorganisms (Fig. 4). In the cases without metal addition, the addition of the adsorbants increased the SOUR by 40%. The added adsorbants may increase the probabilities for substrates and microorganisms to come closer to each other. Both the substrates and microorganisms adhered on the adsorbants and this enabled the substrates to be degraded by microorganisms more easily than in suspended form. With heavy metal addition, the added adsorbants were able to reduce the toxicity of heavy metals by PAC-metal or dried sludge-metal adsorption. Thus it increased the bio-oxidation processes of microorganisms in activated sludge and subsequently increased the oxygen uptake rate. The addition of powdered activated carbon was

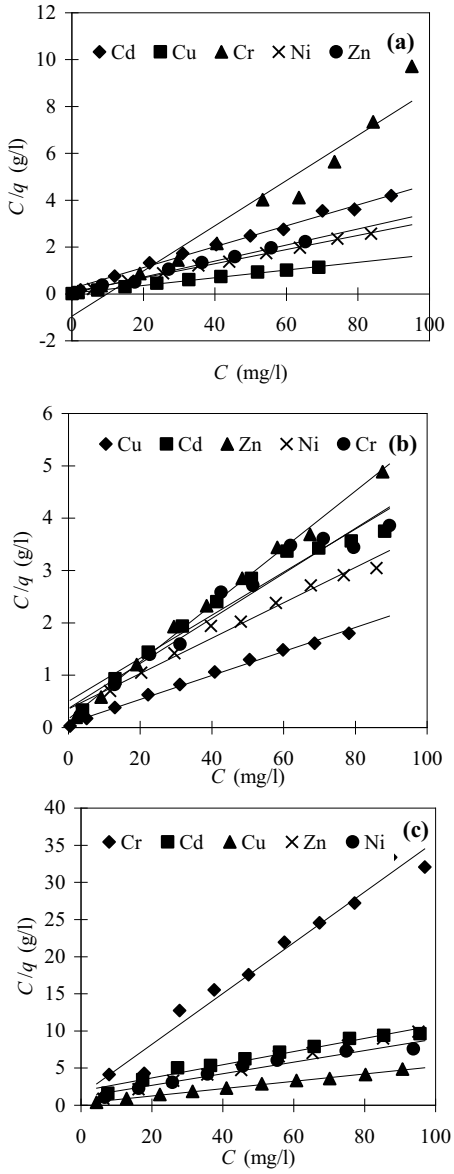

Fig. 2 Langmuir isotherms for (a) PAC, (b) activated sludge and (c) dried sludge for heavy metals adsorption.

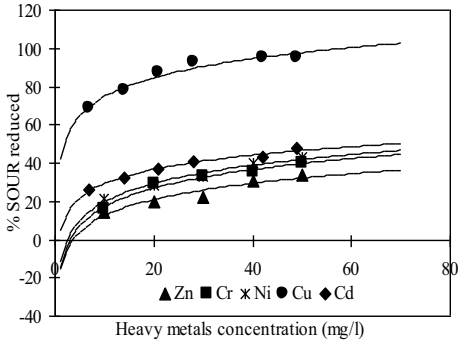

Fig. 3 Effects of heavy metals on specific oxygen uptake rate by activated sludge microorganisms.

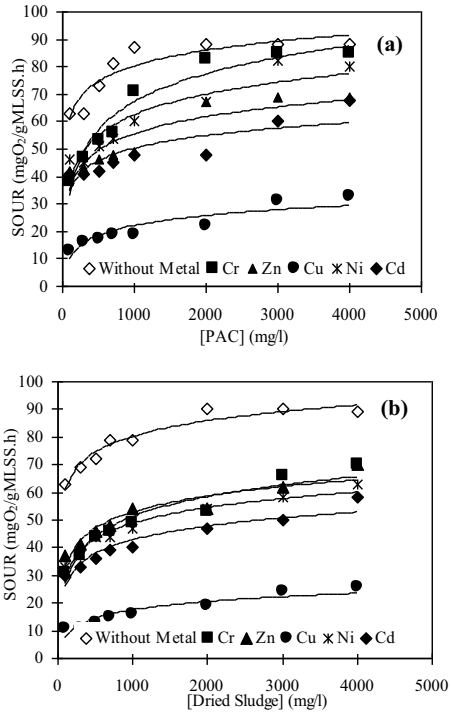

Fig. 4 Effects of (a) PAC and (b) dried sludge on oxygen uptake by activated sludge microorganisms with 35 mg/l of heavy metals.

able to increase the SOUR more than dried sludge due to the higher adsorption capacity in heavy metal adsorption.

CONCLUSIONS

Heavy metal adsorption experiments performed on activated sludge and dried sludge reveal an uptake sequence of Cu $>$ Ni $>$ Cd $\simeq$ Cr $>$ Zn and Cu $>$ Ni $\simeq$ Cd $\simeq$ Zn $>$ Cr, respectively. The adsorption capacities in activated sludge-metal and PAC-metal were higher than dried sludge-metal adsorption. However, activated sludge showed better adsorption capacity of Cr and Cd than PAC. The result indicates that activated sludge could be used as sorbent in removing heavy metals and definitely this would reduce the operation cost in wastewater treatment plant.

SOUR measurement showed the toxicity of heavy metals on activated sludge microorganisms in sequence of decreasing toxicity Cu $>$ Cd $>$ Ni $\simeq$ Cr $>$ Zn, which is in partial contrast to those shown by the

adsorption isotherm. The addition of powdered activated carbon and dried sludge into the base solution with and without heavy metals increased the activated sludge microorganisms SOUR by reducing the toxic effects of heavy metals and acting as reaction site for substrates and microorganisms.

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