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Physical and chemical modification of distillery sludge for Pb(II) biosorption

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Abstract

The waste distillery sludge from sugar-cane industry was pretreated physically (boiled, heated and autoclaved) as well as chemically (HCl, H₂SO₄, H₃PO₄, NaOH, Ca(OH)₂, Al(OH)₃, C₆H₆, HCHO, CH₃OH and Cl₂H₂₅OSO₃Na (sodium dodecyl sulphate (SDS)) for assessing the comparative sorption capacity of untreated and modified distillery sludge for Pb(II) biosorption from aqueous solutions. Experiments were conducted in shake flasks on a batch basis to access the effect of different experimental parameters such as pH, biosorbent dosage, biosorbent size, initial Pb(II) concentration and contact time. The uptake capacity 'q' (mg/g) of untreated and pretreated distillery sludge was in following order: NaOH (51.29 ± 1.21) > HCl (49.82 ± 1.22) > HCHO (49.56 ± 1.14) > H₂SO₄ (47.71 ± 1.20) > HgCl₂ (45.32 ± 1.06) > Ca(OH)₂ (44.01 ± 1.18) > MeOH (43.73 ± 1.23) > C₆H₆ (42.72 ± 1.19) > H₃PO₄ (42.01 ± 1.17) > SDS (40.87 ± 1.27) > autoclaved (40.23 ± 1.24) > Boiled (39.95 ± 1.19) > heated (38.87 ± 1.32) > Al (OH)₃ (38.30 ± 1.14) > untreated (37.76 ± 1.21). In further parameter studies, the optimized biosorbent size was 0.250 mm at pH 5 and best dose was 0.05 g of biosorbent. The applicability of the Langmuir and Freundlich models for sorption process was tested and best fitted model was Langmuir with the coefficient of determination (R^2) value, 0.97, the process followed second order kinetic mechanism.

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1. Introduction

Release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems [1]. Industries such as smelters, metal refineries, and mining operations have been indicated as major sources of metal release into the environment [2–6]. Heavy metal contamination that does get into the environment could cause permanent negative ecological effects [6]. Pb(II) is a potent neurotoxic metal when present above 0.05 mg/L in drinking water [7]. Conventional technology for removing metals from solutions includes precipitation in the form of oxides, hydroxides, carbonates, or sulphides, and separation by settling. This approach, however, has several limitations, such as inefficient

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0304-3894/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2007.04.110 precipitation when metals are present as anions or are complexes, final concentration imposed by the solubility product, and formation of unsettleable particles [8]. It has long been recognized that adsorption is capable of removing metals in a wider pH range and to much lower levels than precipitation [9-21]. Other more expensive physico-chemical treatments, such as redox reactions or ion exchange, are justified only for particular recoveries. It has been demonstrated that biosorption is a potential alternative to traditional treatment processes of metal ions removal [22-25]. Biosorption utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physico-chemical pathways of uptake [26]. Recent biosorption experiments have focused attention on waste materials which are by-products or the waste materials from large scale industrial operations, e.g. the waste mycelia available from fermentation processes, activated sludge from sewage treatment plants [13], biosolids [14], aquatic macrophytes [15], etc. The sugar industry is facing various challenges including deterioration of environment due to its industrial activities. The most important environmental challenge for the sugar mills is associated with solid waste. All the major departments in sugar manufacturing: mill house, process house, and powerhouse and boiler house and for production of industrial alcohol, the distillery stages are responsible for the waste generation. The main source of pollution from distilleries is the spent wash, which is produced as a result of fermentation and distillation of the molasses. The spent wash is acidic in character having very high BOD (40,000-50,000 mg/L) and COD (10,000–125,000 mg/L). The most of solid waste generated by sugar mills are used for land fills. In recent years, considerable attention has been devoted to study the use of industrial wastes as adsorbents [27]. The biological wastes can be further modified to enhance their sorption capacity [2,3]. However, effect of pretreatment on the sorption ability of biosorbents until now is not extensively studied. It has been reported in literature that metal affinity to the biomass can be manipulated by pretreating the biomass with alkalies and acids, which may increase the amount of the metal sorbed [2,3,28,29]. However, there was not single comparative study on effect of physical and chemical pretreatments on uptake capacity of biomass. Moreover, the effect of physical pretreatments and other chemicals such as CH₃OH, HgCl₂, HCHO and C₆H₆ is not reported in literature. In this regard the main objective of present study was to evaluate the effect of pretreatment of distillery sludge for the uptake of Pb(II) from aqueous solutions. The other objectives of this study include identifying the maximum theoretical Pb(II) uptake capacities of the untreated and modified distillery sludge, determining the reaction kinetics and evaluating the effects of various operational parameters such as solution pH, sobent dose, sorbent particle size and initial metal concentration on Pb(II) uptake.

2. Materials and methods

2.1. Biosorbent

Waste distillery sludge samples were collected from Sharkargunj Sugar Mill Jhang, Pakistan. All samples were dried overnight in an oven at 105 °C both before and after pretreatment which provided a biomass source of extended shelf life. The Pb(II) uptake capacity was tested using physical and chemical pretreatment of distillery sludge biomass. Biosorbent was physical modified by heating (heated up to 50 °C in an electrical oven for 24 h), boiling (100 g biosorbent/150 mL water) and autoclaving (at 115 °C for 1 h). For chemical pretreatment, 100 g of finely divided biomass was soaked in 150 mL of 0.1N HCl, H₂SO₄, HNO₃, NaOH, Ca(OH)₂, Al(OH)₃, C₆H₆, HCHO, CH₃OH and C1₂H₂₅OSO₃Na (sodium dodecyl sulphate (SDS)) for 6 h at 150 rpm. The pretreated biosorbents were extensively washed with deionized distilled water (DDW) and filtered thoroughly until a pH 7 ± 0.1 was attained. Finally the resulting biomass was oven dried for 48 h to constant weight. The dried samples were grounded with a laboratory grinder and passed through laboratory vibro-sieving machine (Octagon siever model: OCT-DIGITAL 4527-01) prior to their testing for metal biosorption. The fraction of particles between 0.25 to 1 mm was used in all the experiments.

2.2. Chemicals

All the chemical reagents used in these studies were of analytical grade which were purchased from Fluka Chemicals. The chemicals used in this study include HCl, H₂SO₄, HNO₃, NaOH, Ca(OH)₂, Al(OH)₃, C₆H₆, HCHO, CH₃OH, C1₂H₂₅OSO₃Na (sodium dodecyl sulphate (SDS)), Pb(NO₃)₂ and Pb(II) atomic absorption spectrometry standard solution.

2.3. Batch Pb(II) uptake experiments

All glassware used for experimental purposes was washed in 60% (v/v) nitric acid and subsequently rinsed with deionised water to remove any possible interference by other metals. Stock Pb(II) solution (1000 mg/L) was prepared by dissolving 1.598 g Pb(NO₃)₂ in 100 mL of deionized distilled water (DDW) and diluting quantitatively to 1000 mL using DDW. The pH of stock solution was 4.75. The solutions of different concentrations were prepared by adequate dilution of the stock solution with DDW. Batch tests were carried out in 250 mL shake flasks at 30 °C and 150 rpm up to 24 h. 100 mg/L of Pb(II) ions at pH 5 was initially used at a biomass level 0.5 g/L in order to preliminarily screen the capability of distillery sludge to remove the Pb(II) ions in 100 mL of solution. For adjusting the pH of the medium 0.1N solutions of NaOH and HCl were used. Additional tests were then carried out increasing starting metal concentration, biomass amount, biosorbent particle size and time in order to check the possible maximum removal of Pb(II). Control assay was accompanied with each experiment.

2.4. Analytical procedures

Samples were filtered through 0.2 µm-Millipore filters in order to remove solid particles and then were analyzed to determine the ion concentration by an atomic absorption spectrophotometer (Model: AAnalyst 300, Perkin-Elmer). Sorption capacity "q" is the amount of metal ion (mg) biosorbed per g (dry weight) of biomass. $X_{\rm m}$ ($q_{\rm max}$) is the maximum amount of metal which can be up taken by biosorbent. In simple words, qis the adsorption capacity and its maximum value is known as $q_{\text{max.}}$ Maximum metal sorption capacity (q) was determined by the decrease in metal concentration in the solution after addition of different amounts of biomass and equilibration. The qvalue was calculated using the simple concentration difference method [30]. The initial concentration, C_0 (mg/L) and metal concentrations at various time intervals, C_i (mg/L) respectively, were determined and the metal uptake q (mg metal adsorbed/g adsorbent) was calculated from the mass balance equation (Eq. (1)):

$$q_{\rm e} = \frac{V(C_{\rm i} - C_{\rm e})}{W} \tag{1}$$

where *V* is the volume of the solution in mL and *W* is the mass of the sorbent in g.

2.5. Sorption isotherms

To examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most commonly used. The Langmuir parameters can be determined from a linearized form of equation (Eq. (2)) [31–32] represented by:

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{X_{\rm m}K_{\rm L}} + \frac{C_{\rm e}}{X_{\rm m}} \tag{2}$$

where q_e is metal ion sorbed (mg/g), C_e (mg/L) is the equilibrium concentration of metal ion solution, X_m (q_{max}) and K_L (L/mg) are the Langmuir constants. X_m (q_{max}) is the maximum amount of metal which can be up taken by biosorbent.

Adsorption-partition constants were determined for Pb(II) using the following log form of the Freundlich isotherm [33–34] (Eq. (3)):

$$\log q_{\rm e} = \frac{1}{n} \log C_{\rm e} + \log K \tag{3}$$

where q_e is metal ion sorbed (mg/g), C_e (mg/L) is the equilibrium concentration of metal ion solution, mg/L, *K* and *n* are constants. The constants *K* (mg/g) and 1/*n* were determined by linear regression from the plot of log q_e against log C_e .

2.6. Kinetic models

Kinetic studies of metal adsorption by the biosorbents were developed in order to determine the minimum necessary time to achieve the sorption equilibrium. Two different kinetic models were applied to evaluate the sorption data of Pb(II) onto untreated and pretreated distillery sludge biomass. The lineraized form of pseudo first-order Lagergren model is generally expressed as (Eq. (4)) [29];

$$\log (q_{\rm e} - q) = \left[\log q_{\rm e} - \left\{ \frac{(k_{1,\rm ads}t)}{2.303} \right\} \right]$$
(4)

The pseudo-second-order model is based on the assumption that biosorption follows a second order mechanism. The pseudo-second-order equation (Eq. (5)) is [29];

$$\frac{t}{q} = \frac{1}{k_{2,\text{ads}}q_{\text{e}}^2} + \frac{t}{q_{\text{t}}}$$
(5)

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t the mass of metal at time *t* (min), $k_{1,ads}$ the first-order reaction rate constant of adsorption (per min), $k_{2,ads}$ is the pseudo-second-order rate constant of adsorption (mg/g min).

2.7. Statistical analysis

All data represents the mean of three independent experiments. Error bars shown in figures represents mean \pm S.D. All statistical analysis was done using Microsoft Excel, 2004, version Office Xp (Microsoft Corporation, USA).

3. Results and discussion

3.1. Effect of solution pH

Solution pH is considered as an important parameter affecting biosorption of heavy metal ions [1-3,35-38]. The site dissociation and solution chemistry of the heavy metals such as hydrolysis, complexation by organic and/or inorganic ligands, redox reactions and precipitation are strongly influenced by pH and, on the other side, strongly influence the speciation and the biosorption availability of the heavy metals [39]. A significant increase in Pb(II) uptake per weight of biomass was obtained as the pH increased from 2 to 5 (Table 1). Maximum biosorption capacity of untreated and pretreated distillery sludge was observed at pH 5. Similar results have been reported by other researchers [40,41]. At low pH, the overall surface charge on the biomass cells should be positive, which should prevent the binding of positively charged metal ions. These findings imply that the functional groups on the biomass cell walls and their ionic states at these pHs determine the extent of biosorption. The other important reason is that at lower pH values, the cell wall ligands would be closely associated with the hydronium ions (H_3O^+) that restrict access to ligands by metallic ions as a result of repulsive forces. This repulsion is stronger at lower pH. On increasing pH, more ligands (carrying negative charges) would be exposed with the subsequent attraction of positively charged metal ions. The pH effect may be further explained in relation to the competition effect between the hydronium ions and metal ions. Metal ions that could associate with the cell wall ligands would have to compete with the hydronium ions for the active sites. At low pH values, the concentration of H_3O^+ far exceeds that of metal ions and hence, occupied the binding sites on the cell walls, leaving metal ions unbound. When the pH was increased, the competing effect of hydronium ions decreased and the positively charged metal ions took up the free binding sites. The metal uptake was hence increased [42].

Table 1

Effect of pH on the sorption capacity, q (mg/g) of untreated and pretreated distillery sludge for the uptake of Pb(II)

Biosorbent	pH 2	рН 3	pH 4	рН 5
Untreated	23.91 ± 1.14	25.24 ± 1.11	28.11 ± 1.10	37.76 ± 1.21
Boiled	28.98 ± 1.12	34.13 ± 1.09	37.54 ± 1.22	39.95 ± 1.19
Heated	29.53 ± 1.23	31.49 ± 1.15	33.47 ± 1.31	38.87 ± 1.32
Autoclaved	28.17 ± 1.11	33.72 ± 1.17	36.31 ± 1.15	40.23 ± 1.24
HCl	32.53 ± 1.12	39.41 ± 1.14	45.30 ± 1.23	49.82 ± 1.22
H_2SO_4	31.45 ± 1.15	40.59 ± 1.13	43.29 ± 1.21	47.71 ± 1.20
H ₃ PO ₄	30.32 ± 1.08	37.59 ± 1.13	39.67 ± 1.20	42.01 ± 1.17
NaOH	29.53 ± 1.05	40.62 ± 1.08	47.79 ± 1.07	51.29 ± 1.16
Ca(OH) ₂	30.31 ± 1.12	39.52 ± 1.20	41.27 ± 1.19	44.01 ± 1.18
Al(OH) ₃	27.53 ± 1.14	33.97 ± 1.13	36.75 ± 1.11	38.30 ± 1.14
MeOH	26.14 ± 1.08	34.66 ± 1.17	39.89 ± 1.07	43.73 ± 1.23
HgCl ₂	26.94 ± 1.04	36.54 ± 1.06	40.41 ± 1.21	45.32 ± 1.06
НСНО	27.45 ± 1.11	39.87 ± 1.09	44.19 ± 1.01	49.56 ± 1.14
C ₆ H ₆	25.12 ± 0.19	32.09 ± 1.20	38.88 ± 1.21	42.72 ± 1.19
SDS	26.32 ± 0.09	35.14 ± 1.15	37.53 ± 1.23	40.87 ± 1.27

Experimental conditions: sorbent dose = 0.5 g/L, sorbent particle size = 0.250 mm, initial metal concentration = 100 mg/L, temperature = $30 \degree \text{C}$, shaking speed = 120 rpm, contact time = 24 h.



Fig. 1. Physical and chemical modification of distillery sludge for uptake of Pb(II) from aqueous solutions. Experimental conditions: pH 5, sorbent dose = 0.5 g/L, sorbent particle size = 0.250 mm, initial metal concentration = 100 mg/L, temperature = $30 \degree \text{C}$, shaking speed = 120 rpm, contact time = 24 h.

3.2. Effect of pretreatment on distillery sludge biomass

To evaluate the effect of pretreatment on biomass, 100 mg/L Pb(II) solution was shaken at 120 rpm with 0.5 g/L of biosorbent having size 0.255 mm at pH 5 for 24 h. Uptake capacity of distillery sludge was significantly increased after pretreatment (Fig. 1.). Physical and chemical pretreatments of biomass were resulted in increase in uptake capacity of distillery sludge biomass (Fig. 1). Physical modification of biomass such as boiling and autoclaving remove mineral matter from biomass and introduce more sorption sites on biomass surface. Heating of biomass, results in decomposition of organic matter, which results in increase in biomass metal sorption capacity due to availability of more biosorption sites. The increase was attributed to the exposure of the latent binding sites after pretreatment [43]. Preheating of biomass could cause a loss of amino-functional groups from its surface through the nonenzymic Browning reaction. Amino-functional groups are among the functional groups in the composition of polysaccharides which contribute to the binding of heavy metals [44-46].

Acids can enhance uptake capacity of biomass by increasing the surface area and porosity of original sample [3,29,47]. Bioadsorption capacity was significantly enhanced as a result of alkali pretreatment. Alkali treatment of biomass may destroy autolytic enzymes that cause putrefaction of biomass and remove lipids and proteins that mask reactive sites [48–50]. Removal of impurities from surface and after rupturing of cell-membrane is reason behind the increase in metal uptake capacity of biomass after basic pretreatment [3,48,49,51,52,28]. NaOH treated distillery sludge showed maximum enhancement in biosorption of Pb(II). NaOH pretreatment could rupture the biomass cells which could release polymers such as polysaccharides that have a high affinity towards certain metal ions [52,53,44].

3.3. Effect of biosorbent dose

The influences of the amounts of untreated and pretreated distillery sludge doses are shown in Fig. 2. It can be concluded from obtained results that Pb(II) loading capacity on waste distillery sludge biomass was greatly influenced by the initial concen-



Fig. 2. Effect of biosorbent dosage on removal of Pb(II) from aqueous solutions by untreated and modified distillery sludge. Experimental Conditions: pH 5, sorbent particle size = 0.250 mm, initial metal concentration = 100 mg/L, temperature = $30 \degree \text{C}$, shaking speed = 120 rpm, contact time = 24 h.



Fig. 3. Effect of biosorbent particle size on uptake of Pb(II) from aqueous solutions by untreated and pretreated distillery sludge. Experimental conditions: pH 5, sorbent dose = 0.5 g/L, initial metal concentration = 100 mg/L, temperature = $30 \degree \text{C}$, shaking speed = 120 rpm, contact time = 24 h.

tration of dried biomass used. The maximum Pb(II) adsorption was achieved with a biomass concentration of 0.5 g/L and sorption capacity declined smoothly with increase in biomass level [55]. The decrease in uptake capacity of untreated and modified distillery sludge for Pb(II) removal from aqueous solutions may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area. Similar result has been reported by Pal et al. [54] and Kahraman et al. [55]. With appropriate ratio of biomass quantity per volume of heavy metal (0.5 g of sorbent/litre of metal ion solution, in present case) depuration higher than 80% can be obtained.

3.4. Effect of particle size of biosorbent

The effect of altering the sorbents particle size on the sorption capacity, q (mg/L) is shown Fig. 3. The figure illustrated that the more finely grounded biomass more rapidly up took Pb(II) ions, and the equilibrium was reached faster than those achieved with the large particle sized biomass. This was most probably due to the increase in the total surface area which provided more sorption sites for the metal ions. The enhanced removal of sorbate by smaller particles has been reported previously [1-3,10].

3.5. Effect of initial metal ion concentration

The metal removals by untreated and pretreated distillery sludge corresponding to different initial metal concentrations (25, 50, 100, 200, 400 and 800 mg/L) are shown in Fig. 4. The parameters such as contact time (24 h), volume of solution (100 mL), particle size (0.250 mm) and biomass loading (0.5 g/L) were kept constant. In general, the data revealed that sorption capacity increased with increase in initial metal ion concentration on biosorbent (Fig. 4). This sorption characteristic represented that surface saturation was dependent on the initial metal ion concentrations. The binding sites are limited keeping biomass loadings as constant. On increasing metal concentration, the percentage of metal removed decrease due to diminishing loading capacity of biomass. Data fitted with Langmuir and Freundlich isotherm models is tabulated in Table 2. The R^2 and q_{max} values suggested that the Langmuir isotherm



Fig. 4. Effect of initial metal concentration on sorption of Pb(II) from aqueous solutions by untreated and modified distillery sludge. Experimental conditions: pH 5, sorbent dose = 0.5 g/L, sorbent particle size = 0.250 mm, temperature = $30 \degree \text{C}$, shaking speed = 120 rpm, contact time = 24 h.

Table 2			
Langmuir and	Freundlich isotherm parameters for Pb(II) uptake	e untreated and pretreated distillery slu	ıdge
Biosorbent	Langmuir isotherm parameters	Experimental value	Freundlic

Biosorbent	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters			
	$\overline{X_{\rm m} (q_{\rm max}) ({\rm mg/g})}$	$K_{\rm L}$ (L/mg)	R^2	$q_{\rm max} \ ({\rm mg/g})$	$q_{\rm max} \ ({\rm mg/g})$	<i>K</i> (mg/g)	R^2	1/n
Untreated	71.43	0.0188	0.9833	67.02	66.82	16.25	0.9073	0.2128
Autoclaved	81.30	0.0170	0.9803	75.62	74.63	16.83	0.8981	0.2244
HCl	85.47	0.0235	0.9954	81.04	88.45	16.08	0.9704	0.2565
NaOH	91.74	0.0219	0.9838	87.14	84.94	24.91	0.9079	0.1851
HCHO	85.47	0.0189	0.9802	81.74	75.85	24.29	0.8907	0.1717
SDS	74.63	0.0228	0.9928	70.82	70.81	19.31	0.9196	0.1957

Experimental conditions: pH 5, sorbent dose = 0.5 g/L, sorbent particle size = 0.250 mm, initial metal concentration = 25-800 mg/L, temperature = $30 \degree \text{C}$, shaking speed = 120 rpm, contact time = 24 h.

Table 3

Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Pb(II) uptake from aqueous solutions using untreated and pretreated distillery sludge

Pretreated biosorbent with	Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
	$q_{\rm e} ({\rm mg/g})$	$K_{1,ads}$ (min ⁻¹)	R^2	$q_{\rm e} \ ({\rm mg/g})$	$q_{\rm e} ({\rm mg/g})$	$K_{2,ads}$ (g/mg min)	R^2
Untreated	4.29	8.52×10^{-3}	0.7447	37.76	38.02	7.28×10^{-3}	0.9995
Autoclaved	4.15	5.98×10^{-3}	0.7939	40.23	40.49	6.50×10^{-3}	0.9992
HCl	4.59	6.91×10^{-3}	0.6882	49.82	50.25	6.25×10^{-3}	0.9995
NaOH	12.13	1.35×10^{-2}	0.9625	51.29	52.35	3.17×10^{-3}	0.9996
НСНО	12.84	1.75×10^{-2}	0.9570	49.56	50.76	3.34×10^{-3}	0.9999
SDS	8.92	1.12×10^{-2}	0.9361	40.87	41.67	3.62×10^{-3}	0.9992

Experimental conditions: pH 5, sorbent dose = 0.5 g/L, sorbent particle size = 0.250 mm, initial metal concentration = 100 mg/L, temperature = $30 \degree \text{C}$, shaking speed = 120 rpm, contact time = up to 24 h.

describes the sorption process well as compared to model of Freundlich.

3.6. Kinetic study for metal binding to distillery sludge

The experiments were conducted to determine the time required for distillery sludge to bind the Pb(II) ions. The Pb(II) ion uptake was rapid within first 30 min followed by slow sorption till equilibrium was reached. From this sorption behavior of distillery sludge it can be concluded that Pb(II) ions uptake by waste distillery sludge biomass followed a two-step mechanism where the metal ion was physically/chemically up taken onto the surface of the biosorbent before being taken up into the inner adsorption sites of dead cells [56,57]. The first step, known as a passive surface transport, took place quite rapidly, i.e. within 30 min whilst the second passive diffusion step transport, could take much longer time to complete [10,17,58]. The fast metal uptake (within first 30 min) observed for distillary sludge is of particular importance to process design and operation in practical uses. The mechanism of biosorption and potential rate controlling steps, such as mass transport and chemical reaction procedures, must be investigated to properly understand adsorption kinetics. When the biomass is employed as a free suspension in a well-agitated batch system, the effect of external film diffusion on biosorption rate can be assumed not significant and ignored in any kinetic analysis.

A comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models are tabulated in Table 3.

The second-order rate model has received considerable attention as a tool for quantitatively predicting the uptake of metals from aqueous solutions. In addition to high value of coefficient of determination (R^2), a close agreement between experimental and estimated q_e values suggests that sorption process followed second order mechanism. In this model, the rate-limiting step is a biosorption mechanism involving chemisorption, where metal removal from solution is due to purely physico-chemical interactions between biomass and metal solution [59].

4. Conclusions

The biosorption of Pb(II) using dried untreated and pretreated distillery sludge biomass was evaluated here. The Pb(II) sorption was found dependent on solution pH, biosorbent particle size, biosorbent dosage, initial concentration of metal ion being sorbed and contact time. The pretreatment of biomass resulted in significant increase in sorption capacity. Furthermore, chemical modifications of distillery sludge were found more effective in comparison to physical pretreatments. The sorption isotherms followed the Langmuir type suggesting monolayer sorption character. The sorption of Pb(II) ions rapidly occurred within first 30 min followed by slow diffusion controlled step till the equilibrium was reached. This work illustrated an alternative solution for the management of the distillery sludge (an industrial waste and unwanted biological material) as biosorbent for the removal of Pb(II) from aqueous streams.

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References

- M.A. Hanif, R. Nadeem, H.N. Bhatti, N.R. Ahmad, T.M. Ansari, Ni(II) biosorption by *Cassia fistula* (Golden Shower) biomass, J. Hazard. Mater. B 139 (2007) 345–355.
- [2] M.N. Zafar, R. Nadeem, M.A. Hanif, Biosorption of nickel from protonated rice bran, J. Hazard Mater. B 143 (2007) 478–485.
- [3] H.N. Bhatti, B. Mumtaz, M.A. Hanif, R. Nadeem, Removal of Zn(II) ions from aqueous solution using *Moringa oleifera* Lam. (horseradish tree) biomass., Process Biochem. 42 (2007) 547–553.
- [4] K. Conrad, H.C.B. Hansen, Sorption of zinc and lead on coir, Bioresour. Technol. 98 (2007) 89–97.
- [5] S.K. Papageorgiou, F.K. Katsaros, E.P. Kouvelos, J.W. Nolan, H.L. Deit, N.K. Kanellopoulos, Heavy metal sorption by calcium alginate beads from *Laminaria digitata*, J. Hazard. Mater. B137 (2006) 1765–1772.
- [6] T. Akar, S. Tunali, Biosorption characteristics of Aspergillus flavus biomass for removal of Pb(II) and Cu(II) ions from an aqueous solution, Bioresour. Technol. 97 (2006) 1780–1787.
- [7] Y. Sag, D. Ozer, T. Kutsal, A comparative study of the biosorption of Lead(II) ions to Z. ramigera and R.arrhizas, Process Biochem. 30 (1995) 169–174.
- [8] M.M. Benjamin, R.S. Sletten, R.P. Bailey, T. Bennett, Sorption and filtration of metals using iron-oxide-coated sand, Water Res. 30 (1996) 2609–2620.
- [9] E. Tokcaer, U. Yetis, Pb(II) biosorption using anaerobically digested sludge, J. Hazard. Mater. B137 (2006) 1674–1680.
- [10] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu²⁺, Cd²⁺, Pb²⁺, and Zn²⁺ using dried marine green macroalga *Caulerpa lentillifera*, Bioresour. Technol. 97 (2006) 2321–2329.
- [11] A. Hammaini, F. González, A. Ballester, M.L. Blázquez, J.A. Muňoz, Biosorption of heavy metals by activated sludge and their desorption characteristics, J. Env. Manage. 84 (2007) 419–426.
- [12] J. Yu, M. Tong, X. Sun, B. Li, Cystine-modified biomass for Cd(II) and Pb(II) biosorption, J. Hazard. Mater. 143 (1-2) (2007) 277–284.
- [13] A. Hammaini, Stimulus uptake of metals by activated sludge, Mineral. Environ. Eng. 16 (2003) 723–729.
- [14] N. Lisa, B. Kanagaratnam, M. Trevor, Biosorption of Zinc from aqueous solutions using biosolids, Adv. Environ. Res. 8 (3-4) (2004) 629–635.
- [15] O. Keskinkan, M.Z. Gosksu, M. Basibyerk, C.F. Forester, Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllurm demersum*), Bioresour. Technol. 92 (2) (2004) 197–200.
- [16] A.A. Abia, M.Jnr. Horsfall, O. Didi, The use of chemically modified and unmodified cassava waste for the removal of Cd Cu and Zn ions from aqueous solution, Bioresour. Technol. 90 (3) (2003) 345–348.
- [17] K.C. Sekhar, C.T. Kamala, N.S. Chary, Y. Anjaneyulu, Removal of heavy metals using a plant biomass with reference to environmental control, Int. J. Mineral. Proc. 68 (2003) 37–45.
- [18] M.S. Hoon, C.S. Park, Y.J. Kim, Y.I. Park, Biosorption isotherms of Pb(II) and Zn(II) on Pestan, an extracellular polysaccharide, of *Pestalotiopsis* sp KCTC 8637P, Process Biochem. 41 (2) (2006) 312–316.
- [19] H. Hussein, I.S. Fbrahim, K. Kandeel, H. Moawad, Biosorption of heavy metals from waste water using *Pseudomonas* sp., E. J. Biotechnol. 7 (1) (2004) 38–46.
- [20] M.T.K. Tsui, K.C. Cheung, N.F.Y. Tam, M.H. Wong, A comparative study on metal sorption by brown seaweed, Chemosphere 65 (2006) 51–57.
- [21] G. Guibaud, E. van Hullebusch, F. Bordas, Lead and cadmium biosorption by extracellular polymeric substances (EPS) extracted from activated sludges: pH-sorption edge tests and mathematical equilibrium modeling, Chemosphere 64 (2006) 1955–1962.
- [22] Y. Liu, X. Chang, Y. Guo, S. Meng, Biosorption and preconcentration of lead and cadmium on waste Chinese herb Pang Da Hai, J. Hazard. Mater. B135 (2006) 389–394.

- [23] A.H. Hawari, C.N. Mulligan, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, Bioresour. Technol. 97 (2006) 692–700.
- [24] A. Pal, S. Ghosh, A.K. Paul, Biosorption of cobalt by fungi from serpentine soil of Andaman, Bioresour. Technol. 97 (2006) 1253–1258.
- [25] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (12) (2007) 2243–2257.
- [26] S. Tunali, A. Çabuk, T. Akar, Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil, Chem. Eng. J. 115 (2006) 203–211.
- [27] R. Sudha Bhai, T.E. Abraham, Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*, Bioresour. Technol. 79 (2001) 73–81.
- [28] A. Kapoor, T. Viraraghvan, Biosorption of heavy metals on Aspergillus niger: effect of pretreatment, Bioresource. Technol. 63 (1998) 109– 113.
- [29] C. Moreno-Castilla, F. Carrasco-Marin, F.J. Maldonado-Hodar, J. Rivera-Utrilla, Effects of non-oxidant and oxidant acid treatments on the surface properties of an activated carbon with very low ash content, Carbon 36 (1997) 145–151.
- [30] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Progr. 11 (3) (1995) 235–250.
- [31] S.K. Bajpai, S. Sharma, Investigation of swelling/degradation behaviour of alginate crosslinked with Ca²⁺ and Ba²⁺ ions, React. Funct. Polym. 59 (2004) 129–140.
- [32] Z. Aksu, Equilibrium and kinetic modeling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, Sep. Purif. Technol. 21 (2001) 285–294.
- [33] A.W. Adamson, Physical Chemistry of Surfaces, 5th ed., John Wiley and Sons, New York, NY, 1990.
- [34] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res. 37 (2003) 4311–4330.
- [35] J.T. Matheickal, I. Lyengar, C. Venkobachar, Sorption and desorption of Cu(II) by *Ganoderma lucidum*, Water Pollut. Res. J. Canada 26 (1991) 187–200.
- [36] J.T. Matheickal, Q. Yu, Biosorption of lead from aqueous solutions by marine alga *Ecklonia radiata*, Water Sci. Technol. 34 (1996) 1–7.
- [37] J.T. Matheickal, Q. Yu, Biosorption of heavy metals from waste water using Australian biomass, Dev. Chem. Mineral. Process. 5 (1997) 5–20.
- [38] E. Fourest, C. Canal, J.C. Roux, Improvement of heavy metal biosorption by mycelial dead biomasses (*Rhizopus arrhizus, Muchor miehei*, and *Pencillium chrysogenum*): pH control and cationic activation, FEMS Microbiol. Rev. 14 (1994) 325–332.
- [39] A. Özer, D. Özer, Comparative study of the biosorption of Pb(II) Ni(II) and Cr(VI) ions onto *S. cerevisiae*: determination of biosorption heats, J. Hazard. Mater. B100 (2003) 219–229.
- [40] I. Tüzün, G. Bayramoğlu, E. Yalçın, G. Başaran, G. Çelik, M.Y. Arıca, Equilibrium and kinetic studies on biosorption of Hg(II) Cd(II) and Pb(II) ions onto microalgae *Chlamydomonas reinhardtii*, J. Environ. Manage. 77 (2005) 85–92.
- [41] D.K. Singh, D.P. Tiwari, D.N. Saksena, Removal of lead from aqueous solutions by chemically treated used tea leaves, Indian J. Environ. 35 (3) (1993) 169–177.
- [42] S. Schiewer, B. Volesky, in: D.R. Lovley (Ed.), Environmental Microbe-Metal Interactions, ASM Press, Washington, DC, 2000, pp. 329– 362.
- [43] M. Galun, E. Galun, B.Z. Siegel, P. Keller, H. Lehr, S.M. Siegel, Removal of metal ions from aqueous solutions by *Penicillum* biomass: kinetic and uptake parameters, Water Air Soil Poll. 33 (1987) 359–371.
- [44] M. Loaec, R. Olier, J. Guezennec, Uptake of lead, cadmium and zinc by a novel bacterial expolysaccharide, Water Res. 31 (5) (1997) 1171–1179.
- [45] R. Whistler, T.R. Daniel, Carbonhydrates, in: O.R. Fennema (Ed.), Food Chemistry (1985) 96–105.
- [46] G. Yan, T. Viraraghavan, Effect of pretreatment on the bioadsorption of heavy metals on *Mucor rouxii*, Water SA 26 (1) (2000) 119–124.
- [47] B. Benguella, H. Benaissa, Cadmium removal from aqueous solution by chitin: kinetic and equilibrium studies, Water Res. 36 (10) (2002) 2463–2474.

- [48] W.J. McGahren, G.A. Perkinson, J.A. Growich, R.A. Leese, G.A. Ellestad, Chitosan by fermentation, Process Biochem. 19 (1984) 88–90.
- [49] J.A. Brierley, C.L. Brierley, R.F. Decker, G.M. Goyack, European patent application No. 85112810, Publication No. 0 181 497 (1985).
- [50] T.R. Muraleedharan, C. Venkobachar, Mechanism of cobalt biosorption, Biotechnol. Bioeng. 33 (1990) 823–831.
- [51] T.R. Muraleedharan, C. Venkobachar, Mechanism of biosorption of copper(II) by *Ganoderma lucidum*, Biotechnol. Bioeng. 35 (1990) 320–325.
- [52] M.W. Mittleman, G.G. Geesey, Copper binding characteristics of exopolymers from a freshwater sediment bacterium, Appl. Environ. Microbiol. 49 (1985) 846–851.
- [53] J.M. Dow, P.H. Rubery, Chemical fraction of the cell walls of mycelial and yeast-like forms of *Mucor rouxii*: a comparative study of the polysaccaride and glycoprotein components, J. Gen. Microbiol. 99 (1977) 29–41.
- [54] A.A. Pal, S. Ghosh, A.K. Paul, Biosorption of cobalt by fungi from serpentine soil, Bioresour. Technol. 97 (2006) 1253–1258.

- [55] S. Kahraman, D. Asma (Hamamci), S. Erdemoglu, O. Yesilada, Biosorption of copper(II) by live and dried biomass of the white Rot fungi *Phane-rochaete chrysosporium* and *Funalia trogii*, Eng. Life Sci. 5 (1) (2005) 72–77.
- [56] B. Volesky, Biosorption of Heavy Metals, CRC Press, Boca Raton, 1990.
- [57] H. Kojima, K.Y. Lee, Photosynthetic Microorganisms in Environmental Biotechnology, Springer-Verlag Hong Kong Ltd., Hong Kong, 2001.
- [58] K.C. Sekhar, C.T. Kamala, N.S.A. Chary, R.K. Sastry, T.N. Rao, M. Vairamani, Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass, J. Hazard. Mater. 108 (2004) 111–117.
- [59] Z. Aksu, Equilibrium and kinetic modelling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, Sep. Purif. Technol. 21 (2001) 285–294.