Comparison of Adsorption Characteristics of Waste Biomass Materials for the Removal of Pb ions from Industrial Effluents

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Abstract: Adsorption of lead ions from aqueous solutions onto various waste biomass materials was studied. Coir pith, saw dust, rice husk, rice bran and tea waste were tested for Pb ion adsorption to enable comparison with alternative commonly used adsorbent granular activated carbon. Batch experiments were conducted to determine the adsorption capacities and kinetics of the process. All the waste biomass materials tested were capable of binding appreciable amounts of Pb ions from aqueous solutions. Adsorption capacities were in the order, coir pith > tea waste > activated carbon > rice bran > saw dust > rice husk. The equilibrium data were satisfactorily fitted to Langmuir and Freundlich isotherms. Langmuir monolayer adsorption capacities for coir pith, tea waste and granular activated carbon were 72, 65 and 28 mg/g respectively. Kinetic studies revealed that Pb uptake was fast with 90% or more of the adsorption occurring within first 15 to 20 min of contact time. The kinetic data fits to pseudo second order model with regression coefficients greater than 0.99. Fixed bed column experiments were performed to study practical applicability and breakthrough curves were obtained. Column operations showed lower adsorption capacities than the batch operation. Amount of Pb adsorbed in the column operations were 46, 41 and 19 mg/g for tea waste, coir pith and granular activated carbon respectively.

Key words: Lead, adsorption, waste biomass

1. Introduction

Heavy metals are continuously released into the water streams from industrial processes. Lead, finds extensive applications in day-to-day commodities like batteries, paints, ceramics, soldering etc. It is an essential component for production of many other highly technical products. Water streams get contaminated with lead, due to inappropriate waste disposal practices. Lead is a very toxic element even at low concentrations. It affects the central nervous system, kidneys, gastrointestinal system etc [1-4]. Due to the increased awareness about environmental and health aspects many countries have imposed stringent environmental laws and treatment of the effluent streams has got exceptionally great importance nowadays [5].

There are various established methods for the removal of heavy metals [1]. Generally, the techniques employed include reduction and precipitation, coagulation, flotation, adsorption on activated carbon, ion-exchange and membrane filtration processes. Precipitation followed by coagulation has been extensively employed for the removal of heavy metals from

water. However, this process usually produces large volumes of sludge consisting small amounts of heavy metals. Membrane filtration is a proven way to remove metal ions but its high cost limits the use in practice. Activated carbon has been tested for heavy metal ion removal by many workers [6-10]. Alternative methods like adsorption on agricultural waste have been employed by many researchers [11-31]. Plant residuals which are mainly comprise of cellulose materials can adsorb heavy metal cations in aqueous medium. Adsorption of heavy metal ions occurs as a result of physicochemical interaction, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface [4, 19, 26, 28, 32, 33, 34, 35]. Adsorption capacities and kinetics depend on the operating conditions such as solution pH, particle size, metal concentration and adsorbent dose and the pretreatments given to the waste material [12-16, 24, 25]. The surface properties of the waste biomass can be improved by various thermal and chemical treatments given to the adsorbent

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prior to adsorption [13-17, 21, 22, 24, 25]. However, this may incur cost and also lead to addition of other chemicals to the water. Literature shows that waste biomass materials have good adsorption capacities for other metal ions such as Ni, Cd, Cr, Cu and Zn [6, 7, 12, 21, 29].

This work investigates and compares the potential of commonly available waste biomass materials in Sri Lanka in removal of lead ions from aqueous solutions. Coir pith, rice husk, rice bran, saw dust and tea waste were used as waste biomass materials. The adsorption characteristics of waste biomass materials were compared with that of commonly used adsorbent granular activated carbon. Batch experiments and fixed bed column tests were conducted to determine adsorption kinetics, equilibrium data and the adsorption capacities.

2. Materials and Methods

2.1. Preparation of the adsorbent

Rice husk (RH), rice bran (RB), saw dust (SD) and coir pith (CP) were obtained from Sri Lankan mills. Tea waste (TW) was obtained from Sri Lankan black tea. Soluble and coloured components were removed from the bio mass by washing with hot water at 80 °C. This was repeated until the water was virtually colourless. The bio mass were then washed with distilled water and were oven dried for 12 hrs at 85 °C. The dried materials were sieved and stored in sealed polythene bags. The fraction between 350-850 μ m was used for all the experiments. Coconut shell based Granular Activated Carbon (GAC) provided by Haycarb Ltd, Sri Lanka was used as a benchmark adsorbent for comparison with bio mass. The GAC was used at the original size, 1298 μ m, without any size reduction.

2.2. Synthetic waste water preparation

Synthetic wastewater solutions were prepared by dissolving analytical grade $Pb(NO_3)_2$ in distilled water to obtain 1000 mg of metal/L solutions. The solution was diluted to the required concentration for experiments. Our previous work and other work reported in literature on adsorption of heavy metal ions [18, 20, 27, 34, 36] have shown that biomass

materials possess highest adsorption above pH 5. The pH of the solution was measured and observed as 5.5(0.5) and no chemicals were added to change pH.

2.3. Adsorption tests

Batch adsorption tests were conducted by mixing known weight of adsorbent and solution of known metal-ion concentration. The mixture was shaken in a mechanical shaker and samples of solution were withdrawn from the bottle at known time intervals and analyzed for the metal ion using atomic absorption spectrophotometer.

Fixed bed column adsorption experiments were conducted in a small 3 cm diameter glass column. The column was filled with a known weight of adsorbent to obtain the required bed height. The metal ion solution containing 100 mg/L of Pb was fed to the column at a constant flow rate through the bed using a peristaltic pump. The solution leaving the bottom of the column was collected at various time intervals and the samples were analyzed for lead. The solution pH was at 5.5 ± 0.5 and all the experiments were conducted at room temperature 22 ± 2 °C.

The batch and column adsorption experiments were performed in duplicate to observe the reproducibility and the mean value was used for each set of values.

2.4. Metal analysis and adsorbent characterization

Atomic absorption spectrophotometer with an air-acetylene flame and hollow cathode lamps for Pb was used for metal ion analysis. The absorbance of the samples was read in triplicate. True and bulk densities of adsorbents were also determined using the specific gravity bottle method. The particle size was measured by sieve analysis. The surface area and pore size of selected adsorbents (tea waste, coir pith and activated carbon) were measured using BET surface area analyzer (Micromeritics, Tri star 3000).

3. Results and Discussion

Physical properties of adsorbents determined as described above are listed in Table 1.

The metal ion concentrations obtained for batch experiments were converted to percentage of

metal ion removed and amount of metal adsorbed per unit weight of adsorbent. Errors due to filtration were corrected using a calibrated curve obtained by filtering solutions of known concentrations through the filter paper and analyzing the solution for Pb concentration. The results thus obtained are presented and discussed in this section.

3.1. Adsorption capacities

Fig. 1 shows the amount of metal ions adsorbed per unit weight of adsorbent (q), coir pith and tea waste showed highest adsorption capacities (20 mg/g) whereas rice husk showed the lowest 5.75 mg/g. Despite the high surface area GAC showed 14.4 mg/g adsorption. Biomass materials are mainly comprised of cellulose materials that can adsorb heavy metal cations in aqueous medium. Adsorption of lead cations occurs as a result of physicochemical interaction, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface. Therefore the adsorption capacity depends on the type of functional groups available on the biomass material.

Fig. 2 compares the percentage removal of Pb as a function of time for all adsorbents tested. The experimental results show rapid initial adsorption followed by a slower rate. Initially, the adsorption sites are open and the metal ions interacts easily with the site and hence a higher rate of adsorption is observed. Further, the driving force for adsorption -the concentration difference between the bulk solution and the solid-liquid interface- is higher initially and this

results a higher adsorption rate. However, after the initial period slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent. Results showed that 100% removal of Pb was possible with the dose of 5 g/L for CP and TW. Higher doses are required for 100% removal of lead when other adsorbents are used.

Figure 1: Comparison of adsorption capacities of Pb onto various adsorbents: 0.5 g of adsorbent mixed with 100 ml of 100 ppm solution at 22 °C.

Figure 2: Percentage of Pb adsorption as a function of time for various adsorbents, 1 g of adsorbent mixed with 200 ml of 100 ppm solution at 22 °C.

Table 1: Physical properties of adsorbents

Property	Tea waste	CP	GAC	RH	RB	SD
mean diameter (μm)	600	513	1298	593	465	580
Surface area (m^2/g)	0.79	1.56	683.14	-	-	-
Pore size (nm)	1.92	4.52	2.28	-	-	-
Bulk density (kg/m^3)	206	116	470	205	193	134
True density (kg/m^3)	1106	799	1755	1025	963	668

Table 2: Second order kinetic parameters for adsorption of Pb onto various adsorbents. (100 ppm, 5 g of adsorbent/L, 22 °C)

Adsorbent	Amount adsorbed predicted - q_{pre} (mg/g)	Amount adsorbed Experimental - q_{exp} (mg/g)	Initial adsorption rate-h ($\text{mg g}^{-1} \text{min}^{-1}$)	Rate constant - k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Rice husk	7.26	7.19	10	0.1811	1
saw dust	8.93	8.76	6	0.0754	0.9999
coir pith	20.08	19.95	35	0.0861	1
Rice bran	10.79	10.63	10	0.0853	0.9999
Tea waste	20.28	19.81	12	0.0284	0.9998
GAC	14.79	14.4	4	0.0172	0.9974

Table 3: Isotherms for Pb adsorption onto CP, TW and GAC at 22 (C.

Adsorbent	Freundlich Isotherm		Langmuir Isotherm	
	Equation (6)	R ²	Equation (5)	R ²
Coir pith	$q_e = 15.03C_e^{0.3845}$	0.8943	$\frac{1}{q_e} = \frac{1}{12.75C_e} + \frac{1}{71.9}$	0.9842
Tea waste	$q_e = 9.65C_e^{0.3885}$	0.9614	$\frac{1}{q_e} = \frac{1}{3.23C_e} + \frac{1}{65.4}$	0.9579
GAC	$q_e = 3.54C_e^{0.4605}$	0.9266	$\frac{1}{q_e} = \frac{1}{1.94C_e} + \frac{1}{27.8}$	0.8623

Table 4: Langmuir constants (qo) reported in literature for adsorption of Pb onto various types of waste biomass without any chemical or thermal treatment.

Adsorbent	q _o (mg/g)	Ref
Saw Dust	3	Shukla [19]
Rice Husk	11	Chuah [12]
Peach Stone	0.0023	Rashed [42]
Apricot Stone	0.0013	
Cocoa Shells	33	Meunier [35]
Tree Leaves	21	Baig [22]
Tree Barks	21	Martin Dupoint [23]
Wheat bran	64	Farajzadeh [43]
Sago Waste	47	Quek [44]
Coir pith	72	This work
Tea waste	65	
GAC	28	

3.2. Adsorption kinetics

Adsorption kinetics controls the solute uptake rate which, in turn, controls the length of the mass transfer zone within a contactor, and (indirectly) affects the size of the adsorption equipment. Several adsorption kinetic models have been developed, and widely used, to describe adsorption kinetics [8, 10, 37, 38, 39, 40]. The Lagergren pseudo-first-order model can be expressed as:

$\frac{dq}{dt} = k_1(q_e - q)$ (1)

$\ln(q_e - q) = \ln(q_e) - k_1t$ (2)

Where q is the capacity at time (t), q_e is the equilibrium capacity, and k₁ is the pseudo-first-order adsorptive rate constant.

Alternatively, the second-order model is expressed as:

$\frac{dq}{dt} = k_2(q_e - q)^2$ (3)

$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2q_e^2}$ (4)

Where k₂ is the second-order rate constant. The initial adsorption rate (h) is equal to k₁q_e and k₂q_e² (mg g⁻¹ min⁻¹) for first- and second-order models, respectively.

These models were used to analyze the nature of the adsorption kinetics for Pb on adsorbents. Specifically, the results obtained for adsorption of Pb onto CP, RH, RB, SD, TW and GAC were fitted to both Eq. 2 (pseudo-first order) and Eq. 4 (second order). The results showed that the second-order model, given by Eq. 4. provides better correlation than pseudo-first-order model as shown in Fig. 3.

The corresponding second-order kinetic parameters, and correlation coefficients, thus obtained are shown in Table 2. Experimentally determined sorption capacities shown in the 3rd column of the Table 2 are in agreement with the equilibrium sorption capacities q, determined using second order model. Coir pith showed the highest initial adsorption rate and GAC showed the lowest. Highest rate constant was observed for RH despite the adsorption capacity was lowest.

Figure 3: Pseudo-second order kinetics of Pb onto various adsorbents at 22 °C.

3.3. Adsorption Isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships [41]. Langmuir and Freundlich isotherms are widely used. For solid-liquid systems the linear form of the Langmuir isotherm can be expressed by the equation (5).

$$\frac{1}{q_e} = \frac{1}{bq_0C_e} + \frac{1}{q_0} \quad (5)$$

Freundlich isotherm model is the empirical model for adsorption and expressed as:

$$q_e = kC_e^{1/n} \quad (6)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium, q_0 is the amount of solute adsorbed per unit weight of adsorbent corresponding to complete coverage of available sites. C_e is the residual liquid phase concentration at equilibrium, b is the adsorption coefficient. k and n are constants related to adsorption capacity and adsorption intensity.

Adsorption isotherms were obtained for selected adsorbents, TW, CP and GAC. Adsorption isotherms for Pb (q_e vs C_e) are shown in Fig.4. The experimental data were fitted to both Langmuir and Freundlich isotherms given by equations 5 and 6. The isotherm equations for adsorption of Pb onto TW, CP and GAC and the regression coefficients (R_2) are given in Table 3. $1/n$ values for all three adsorbents lie between zero and 1 indicating favorable adsorption.

Many workers have investigated on other waste biomass as low cost adsorbents for metal ion removal. Langmuir constants, q_0 values obtained for adsorption of Pb onto various other biomass types reported in the literature are listed in Table 4. These values are in the same order of magnitude of the results obtained by this work.

Figure 4: Adsorption isotherms for Pb onto selected adsorbents at 22 °C (Eqⁿ 6).

3.4. Fixed bed adsorption

Fixed bed columns are widely used in practice for adsorption. Column experiments were conducted to understand the adsorption behavior in fixed bed columns and to determine deviation from batch operations.

Breakthrough curves (Outlet Pb concentration vs amount of solution passed through the bed, expressed as number of bed volumes, N) for Pb adsorption onto tea waste, coir pith and GAC from solutions of concentration 100 mg/L are shown in Fig. 5. Typical 'S' shaped curves were obtained for all experiments. However, results show that when the concentration of the solution leaving the column reaches 85-95 mg/L the concentration changes very slowly and hence the full bed exhaustion is achieved at almost infinite time.

The area above the breakthrough curve is a measure of the bed capacity (BC) and is given by [45].

$$BC = G \int_0^T (C_0 - C) dt \quad (7)$$

N , the number of bed volumes is given by

$$N = \frac{Gt}{V} \quad (8)$$

Where G is the solution rate in L/min, C_0 and C are the inlet metal ion concentration and outlet metal ion concentration in mg/L at time t respectively. T is the actual time required for full bed exhaustion, V is the bed volume.

If the adsorption is infinitely rapid an ideal breakthrough curve will be a step change. Therefore the sharper the breakthrough curve the faster the adsorption rate. The results show that adsorption onto Coir pith and Tea waste are faster compared to that of GAC. These results are in agreement with the kinetic data obtained from batch experiments.

Adsorption capacities in the column operations determined by equation (7), were 46, 41 and 19 mg/g for tea, coir pith and granular activated carbon respectively. These values can be compared with the Langmuir and Freundlich model predictions based on batch experiments. The results are tabulated in the Table 5. Adsorption capacities in column were

approximately 47%, 18% and 32% lower compared to batch experiments for CP, TW and GAC respectively. This deviation can be due to following reasons. In batch experiments the mixture was shaken continuously and good interaction between the solid and solute was achieved. In the fixed bed, adsorbent is packed in the column and surface of the solid particles are in contact with each other and therefore results a less solid-solute interaction.

Figure 5: Breakthrough curves for Pb adsorption onto CP, TW and GAC at 22 °C.

Table 5: Results on adsorption of Pb in fixed bed column (10 cm height, 3 cm diameter, 100 ppm solution concentration)

Adsorbent	Fixed bed column			Model predictions (eq ^m with 100 ppm solution)	
	W't of adsorbent (g)	Flow rate L/m ² s	mg adsorbed/g	Langmuir mg adsorbed/g	Freundlich mg adsorbed/g
Coir	9	0.530	41	88	68
Tea waste	15	0.475	46	58	54
GAC	32	0.475	19	30	24

Further, liquid channeling which results poor solid-metal ion contact and less residence time may occur in the column. Therefore bed adsorption capacities are lower compared to batch operation.

4. Conclusions

Coir pith, Tea waste, saw dust, rice husk and rice bran adsorb appreciable amounts of lead from aqueous solutions. Coir pith and tea waste were superior to other waste biomass types tested. Waste biomass materials are effective and inexpensive adsorbent for removal of lead from aqueous solutions that may be operated in either batch operation or in fixed bed columns. The adsorption rate was rapid over an initial period of time and then decreases gradually. The adsorption kinetics fit to pseudo second order model, which is based on the assumption chemisorption is the rate limiting step. The equilibrium isotherms can be represented by both the Freundlich and Langmuir models.

Therefore, biomass materials available in Sri Lanka can be used as a low cost adsorbent for the removal of Pb ions from industrial waste water.

Acknowledgements

Financial assistance from the UK's association of commonwealth universities and Fulbright-Sri Lanka commission are acknowledged. The support from Professors R.A. Williams, J. Raper, C. Adams and D. Ludlow enabling to conduct experiments at University of Leeds, UK and University of Missouri-Rolla, USA are greatly acknowledged.

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