Adsorption Dynamics of Ecofriendly Litter Wastes For Zn(II)/Cr(VI) From Electroplating Effluents - Continuous Column Method

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Abstract

Electroplating industries, play a momentous role in the development and growth of numerous metal manufacturing, but also equally pollute the environment through various means. Most of the electroplating industries operated in Coimbatore are reported under Red category list, their main source of pollution being heavy metal leaching into aquatic streams. The present work deals with the sorption of Zn(II) and Cr(VI) being highly prevalent electroplating effluents. The process of biosorption has many attractive features compared to the conventional effluent treatment methods adopted so far. Batch studies are conducted at varying operating factors to assess the best sorption efficiency amongst the chosen cost effective and eco-friendly materials viz., Mussel Shell Powder (MSP), Prosopis juliflora Bark (PJB), Terminalia catappa Seed Shell (TCSS) and Aegle marmelos correa (AMC). Based on the experimental data the Treated Mussel Shell Powder (TMSP) and Treated Prosopis juliflora Bark (TPJB) are found to be the best sorbent for Zn(II) and Cr(VI) removal respectively. The scaling up process through column experiments are performed to quantify the efficiency of the fixed sorbents under optimized conditions. The long term analysis at the laboratory levels, reveal 100% and 92% metal removal for Zn(II)-TMSP and Cr(VI)-TPJB systems respectively.

Keywords: Electroplating; Effluent; Biosorbents; Column; Coimbatore

Introduction

Industrial sectors expansion involves increased usage of non-biodegradable heavy metals and leading of excess toxic pollutants through liquid effluents. This is an issue of growing concern for humanity and its ecosystem. The wastewaters emanating from such industries viz., plating, tanning, metallurgy require treatment before discharging, but least cared, wherein heavy metal ions like Cr(VI) and Zn(II) are present.

The tolerance limit for Cr(VI) and Zn(II) ions from the effluent discharges into surface waters are 0.1 mg/L and 5.0 mg/L respectively. In potable water, it is 0.05 mg/L and 10.0 mg/L correspondingly [1]. The health risks of Cr(VI) and Zn(II) ions while exceeding the permissible limits results in skin allergy,

liver, stomach problems and also found to be carcinogenic [2]. It is essential to sequester these ions from polluted areas, suggesting suitable methodology.

Various methodologies such as electrochemical, ion exchange, membrane filtration, evaporation, solvent extraction, emulsion pertraction technology, reverse osmosis and chemical coagulation, are available for trapping of heavy metal ions. But these methods possess their own disadvantages, often involving high capital/operational costs and generation of secondary wastes [3, 4].

Biosorption process is one of the efficient methods in trapping toxic metal ions, due to its simplicity, sludge-free operation, easiness in handling, availability of various adsorbents and also efficient removal of heavy metals at lower-concentration levels itself [5]. Biosorbents are prepared from natural waste biomasses that are available in large quantities or certain waste collected from agricultural operations. These low/ no cost materials are reported to have excellent sorption potential that are affordable and eco-friendly.

The current study evaluates the biosorption capacity of litter wastes in trapping Cr(VI) and Zn(II) ions via batch / column method. MSP, PJB, TCSS and AMC were identified, prepared, treated before experimental verification. Removal of heavy metal ions employing the above said eco-friendly materials have not been reported elsewhere in literature.

Materials and Methods

Collection/Treatment of adsorbent materials

The identified litter waste materials Mussel Shell (MSP), Prosopis juliflora Bark (PJB), Terminalia catappa Seed Shell (TCSS) and Aegle marmeloscorrea (AMC) (Figure 1) were collected from localities of Coimbatore, Kangayam, Salem and coastal areas of Tamil Nadu. Collected PJB, MSP and AMC were washed, sun dried, crushed down into small pieces and then sieved. The sieved particles of different mesh sizes for the four materials were treated with 0.1N HCl for 3 hours, washed several

Figure 1: Raw and treated adsorbent materials.

times to neutralize and then air dried. The several washings during neutralization procedure ensure the increase in surface area while soaking the materials. The acid treated Mussel Shell powder (TMSP), Prosopisjuliflora Bark (TPJB), Terminallia cattapa Seed Shell (TTCSS) and Aegle marmeloscorrea (TAMC) were stored in air tight containers.

Chemicals

All the chemicals employed were of Analytical Reagent grade. Doubly Distilled (DD) water was used for preparation and dilutions of solutions. A stock of 1000 ppm metal solutions was prepared by dissolving required amount of $K_2Cr_2O_7$ and $Zn(NO_3)_2$ in 1000 ml of standard flask. The pH of the solutions were adjusted using 0.1N HCl and 0.1N NaOH.

Batch equilibration studies

The equilibration of Cr(VI) and Zn(II) aqueous solutions (50ml volume) with the materials were experimentally verified in a mechanical shaker (KEMI) to define the role of variable parameters viz., particle sizes (0.18mm, 0.24mm, 0.30mm, 0.42mm and 0.52mm) and dosages (200 mg, 400mg, 500mg, 1g, 2g) of the treated adsorbents, initial concentrations of the aqueous Cr(VI) and Zn(II) solutions (100-1000mg/L : 100 mg/L interval), preset time intervals between the sorbent and sorbate species (10-120 minutes : 30 minutes interval), pH of the medium (2,4,7,9 and 11) and temperature (293K-333K : 10 K interval) in order to assess the sorption efficiencies under laboratory conditions. The agitated samples were filtered and the residual metal ion (Cr(VI) and Zn(II)) concentrations were analyzed using Atomic Absorption Spectrophotometer: Shimadzu (AA 6200) (Figure 2) as per standard methods.

All experiments were carried out in duplicate and mean values are presented with the maximum deviation of 2.0%. The percentage removal and amount adsorbed were determined as follows:

$$\text{Removal percentage (\%)} = (C_1 - C_2) / C_1 \times 100$$

$$\text{Amount adsorbed (mg/g)} = (C_1 - C_2) \times V / M$$

where,

C_1 = initial metal concentration (mg/L), C_2 = final metal concentration (mg/L), V= volume (ml) and M= mass of adsorbent (mg).

Results and Discussion

Effect of Particle Size

Tables 1(a)-1(b) show the influence of variable particle sizes of the sorbent materials on the varying systems indicating 0.18mm size to be the favorable size for maximum removal. This is owed to the surface phenomenon, smaller adsorbent size offers larger surface area for metal binding.

Effect of Contact Time/Initial Concentration

The effect of contact time at varying time intervals and that of initial concentrations for the systems are listed in tables 2(a) and 2(b), wherein the registered data indicate the enhancement in amount adsorbed only up to certain metal ion concentrations. This may be of the saturation in the sorption sites on the sorbent as the concentration of the metal ions increased. The varying time intervals for the systems indicate the attainment of equilibrium up to specific contact time, further increase in time interval registered a decline.

Effect of Dosage

The amounts of metal ion adsorbed at different dosages are listed in tables 3(a) & 3(b). The maximum sorptive ability of the materials under varying conditions depict their potentiality as able adsorbents in sequestering heavy metal ions.

Effect of pH

Maximum uptake was observed at pH 2.5 for Cr(VI). At increasing pH environments, a sharp decline in uptake was

observed, which is in good agreement with previous reports. The speciation studies of Cr(VI) in aqueous solution shows that H_2CrO_4 predominates at pH less than 1.0, HCrO_4^- for pH between 1.0 and 6.0 and CrO_4^{2-} at pH above 6. This is due to the electrostatic attraction between the positively charged surfaces of the adsorbent with HCrO_4^- ions. But in highly acidic medium (pH=1.0), H_2CrO_4 (neutral form) is the predominant species of Cr(VI). Hence, percentage removal decreased due to the involvement of less number of HCrO_4^- anions to the positive surface. At higher pH value, the reduction in adsorption may be due to the dual competition of both OH^- and CrO_4^{2-} ions to get adsorbed on the surface of the adsorbent among which OH^- predominates. These results are in agreement with several previous investigations on metal removal by a variety of materials.

The pH dependence for Zn(II) systems registered maximum removal between 5-7; the other ranges exhibit irregular curves. The reason being that at low acidic medium, the H^+ ions compete with the metal ions to get sorbed on the materials and under higher basic conditions metal ions combine with OH^- ions to form respective precipitates.

The optimized conditions resulted from the batch studies for the chosen materials are, Cr(VI) system: 0.18 mm, 200 mg, 1000ppm, 60 min, pH 2.5, 30°C ; Zn(II) system: 0.18 mm, 1.5g,

Figure 2: Atomic Absorption Spectrophotometer Shimadzu (AA 6200).

Adsorbents	Amount Adsorbed (mg/g)				
	0.18 mm	0.24 mm	0.30 mm	0.42 mm	0.71 mm
TTCSS	16.8854	4.335	4.3340	4.542	4.452
TPJB	22.6303	6.876	5.93834	5.826	5.8337
TMSP	13.1202	7.85	6.9756	6.7262	4.3826
TAMC	11.3931	9.384	6.837	6.383	5.3836

Adsorbents	Amount Adsorbed (mg/g)			
	0.18 mm	0.24 mm	0.30 mm	0.42 mm
TTCSS	38.23	28.21	19.74	22.23
TPJB	55.43	44.43	33.17	27.72
TMSP	83.76	25.52	22.29	19.32
TAMC	41.87	34.32	27.28	28.38

Adsorbents	Time (min)	Amount Adsorbed (mg/g)				
		100 ppm	250ppm	500ppm	750ppm	1000 ppm
TTCSS	30	2.7165	3.827	5.726	6.837	5.342
	60	3.9482	5.9147	9.2536	10.5213	16.8854
	120	2.9726	3.98216	6.726	8.8726	10.765
TPJB	30	3.726	4.7236	7.837	10.872	6.865
	60	4.1617	9.9872	15.009	17.921	22.6303
	120	3.5262	5.837	14.763	12.2726	7.976
TMSP	30	0.564	1.987	4.676	4.765	6.876
	60	1.2867	3.4775	8.5776	9.6274	13.1202
	120	0.9875	2.234	6.765	6.9765	10.976
TAMC	30	0.9876	1.234	3.654	4.876	7.9876
	60	2.4485	2.9872	7.1107	7.5983	11.3931
	120	1.2343	1.7654	4.7656	5.764	8.654

Adsorbents	Amount Adsorbed (mg/g)				
	200 mg	300 mg	400 mg	500 mg	1000 mg
TTCSS	16.8854	11.625	10.298	9.937	8.282
TPJB	22.6303	17.2726	15.765	11.7598	10.282
TMSP	7.282	8.2822	9.765	11.272	13.1202
TAMC	11.3931	9.2826	8.875	5.3837	5.3837

Adsorbent	Amount adsorbed (mg/g)				
	100mg	200mg	300mg	500mg	1000mg
TTCS	24.85	26.87	29.76	31.87	38.23
TPJB	11.23	29.87	31.98	37.45	55.43
TMSP	38.65	46.87	52.87	61.87	83.76
TAMC	26.85	33.76	34.98	39.87	41.87

750ppm, 60 min, pH 5.6, 30°C. Further increase in agitation time, beyond the attainment of equilibrium, registered least changes in the residual concentrations of the metal ions. The most suitable adsorbent for maximum removal of Cr(VI) is observed to be TPJB, since it is a natural bio accumulator of Cr(VI) by the transaction of metal to the aerial part of the plant [5]. It is an active transport mechanism and the preferential order being TPJB>TTCSS>TMSP>TAMC. TMSP is found to be best for Zn(II) system, for the reason that the TMSP is more porous in nature when compared to other adsorbents and the preferential order being TMSP>TPJB> TTCSS> TAMC.

Column Studies

The Batch mode studies are the basic pilot studies performed to screen the biosorbents before adopting the adsorption method to the field levels. The results of the Batch equilibration method insist the feasibility and compatibility of the chosen systems for their promising application. Based on batch studies results, column studies were carried out to quantify the adsorbents' efficiencies in the continuous columns' running with the aqueous

Cr(VI) and Zn(II) solutions with TPJB and TMSP respectively [6]. Later, the column schemes are extended to the effluent discharges.

Column packing

The column is made up of cylindrical glass tube, the inner diameter is 2.5 cm and the height is 30 cm. It was packed with sorbent materials between two supporting layers of glass wool, spread with the glass beads at the top of the already packed glass wool layer placed at the bottom. The step by step packing is as: Glass wool layer (3cm thickness), glass beads (2cm thickness), TPJB /TMSP (50/300 g: 6cm height), glass wool (1cm thickness). These materials were loaded from the top of the column and allowed to settle by gravity force. The bottom of the column was fitted with rubber with flow adjustable knob and thus the outflow rate was controlled by adjusting the knob (Figure 5).

1000 mg/L aqueous solutions of Cr(VI) and Zn(II) were prepared and poured from the top of columns slowly and the flow rate through the columns were fixed as 100 ml/5 mins for Cr(VI)-TPJB system and 100ml/20 seconds for Zn(II)-TMSP system after several trials. Maximum removal of 98% and 100% were registered for Cr(VI)-TPJB & Zn(II)-TMSP respectively, after analysis in AAS. The percentage removal was observed to decline upto 90% after passing 20 litres of inlet solutions. Further decline was envisaged upto 30 litres and then the column went exhausted.

Collection of Effluent Samples

Wastewaters containing Cr(VI) and Zn(II) ions above the tolerance levels were found at various electroplating industries located in Kurumbapalayam region of Coimbatore. 10 litres of these effluent samples were collected in pre cleaned PET bottles of 1 litre capacity and analyzed for Cr(VI) and Zn(II) ions of initial concentrations (AAS) after a series of dilutions, Cr(VI): 720 mg/L, Zn(II): 40 mg/L. The pH and conductivity values of the samples were also recorded using LABTRONICS pH meter and conductivity meter respectively (Table 4). Zinc plating bath, the processing, uncoated/ Zn plated materials and the effluents generated are represented in figure 4.

Analysis of Industrial Effluents- Batch/Column Methods

Effluent concentrations of 50 mg/L were fixed for the batch

Table 4: Effluent Samples – Initial Concentrations

S. No	Name of Industries	Cr(VI) (mg/L)	Zn(II) (mg/L)	Conductivity (mv)	pH
1	Unit I	71.52	25.87	21.76	2.3
2	Unit II	695.75	3.398	32.98	1.98
3	Unit III	211	2.817	29.82	2.98
4	Unit IV	6.4647	23.298	87.87	5.35
5	Unit V	5.875	5.876	90.79	0.57
6	Unit VI	449.6	4.383	24.4	1.82
7	Unit VII	720.05	40.08	-0.693	3.45

Figure 3a: Effect of pH - Cr(VI).

Figure 3b: Effect of pH - Zn(II).

Figure 4a: Zinc Plating bath.

Figure 4b: Work at the bath plating.

Figure 4c: Material before plating.

Figure 4d: Material after plating.

Figure 4e: Effluent generated from the bath.

Figure 5: Column packing.

studies and experimentally verified (TPJB and TMSP) under the optimized conditions. The results revealed an appreciable 70% removal of Cr(VI) and Zn(II) ions under batch mode.

sorptive nature of the sorbent materials was quantitatively estimated by the performance of the column studies, on the basis of the long term analysis at the laboratory conditions. The values recorded are 100% and 92% for Zn(II) and Cr(VI) ions respectively.

Conclusion

Batch equilibration method was adopted to analysis the effect of the variables viz., particle sizes and dosages of the adsorbents (TTCSS, TPJB, TMSP, TAMC), initial concentrations of the adsorbate solutions (Zn(II), Cr(VI)), predetermined time intervals between the sorbent - sorbates materials, pH of the solution media and temperatures. TPJB and TMSP were derived to be the best sorbents amongst all the identified materials based on the optimized conditions through batch equilibrium studies. Quantification of these results was justified by column method for the aqueous metal solutions with the fixed sorbent materials. Various electroplating industries located in and around Coimbatore were identified and surveyed for the extent of metal pollution. The effluent samples containing 40mg/L of Zn(II) and 720mg/L of Cr(VI) were collected from Electroplating Industries at Kurumbapalayam area and the performance of the column for these effluent discharges revealed 100% and 92% removal for Zn(II) and Cr(VI) ions respectively. The concluding remarks holds good for TPJB and TMSP to be promising litter waste materials in the sequestering Cr(VI) and Zn(II) ions at field levels.

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