EFFICACY OF MODIFIED TREE BARK IN THE SCREENING OF DIVALENT IONS IN AQUEOUS MEDIA: CHARACTERIZATION AND ISOTHERMAL STUDIES

Gayathri.N.S[1], J. Anuradha[2], N. Muthulakshmi Andal[3]
[1,2]Research Scholar, [3]Assistant Professor,
Department of Chemistry, PSGR Krishnammal College for Women, Coimbatore-4.

Abstract

The present work aims at examining the potentiality of the identified no- cost sorbent *Prosopis juliflora* barks to remove Pb(II) and Cd(II) ions from aqueous solutions. *Prosopis juliflora* barks are collected from Coimbatore, washed with doubly distilled water, dried, pulverized and treated using 0.1N HCl. The characteristics and functional groups present in the treated barks are analyzed by SEM, EDAX and FTIR techniques. Variable parameters influencing the adsorption of divalent ions onto the treated barks are verified by Batch Equilibration method. Effective experimental results are derived under the following optimized conditions: 15 min agitation time, pH 5 environment for the trapping of Pb(II) ions (93% removal) and 20 min agitation time, pH 7 environment for trapping Cd(II) ions (81% removal) at a particle size of 0.18mm, 300 mg dosage and an initial metal concentration of 100 mg/ L. Isothermal analysis of Langmuir and Freundlich models are studied where the best linear fit is exhibited by Langmuir model for both the systems. The obtained results indicate that TPJB is a promising material in chelating Pb(II) in comparison to Cd(II) ions. This shall be attributed to the fact of enlarged ionic radii of Pb(II) ions than Cd(II) ions favoring better sorption in case of the former. Extension of the study is driven towards the applicability of TPJB to sequestrate the heavy metals from industrial outlets.

Keywords: *Prosopis juliflora* bark, characterization, divalent ions, biosorption

Introduction

Pollution of the environment with toxic substances in wastewater effluents is a major concern for public health and environmental quality, with heavy metals being the most dangerous entity[1]. Lead and Cadmium are introduced into water bodies from smelting, metal plating, batteries, mining, pigments, stabilizers, alloy industries and sewage sludge. Lead, one of the three most toxic heavy metals, has long-term potential negative impacts like anemia, encephalopathy, hepatitis and nephritic syndrome[2]. The harmful effects of cadmium include number of acute and chronic disorders such as "itai–itai" disease, renal damage, emphysema, hypertension and testicular atrophy[3]. The removal of these toxic heavy metals from wastewaters is of great interest and important in the field of water pollution control, since metals are persistent and have potential to be bio-accumulated by a range of organisms[4]. Conventional treatment methods have been found to be difficult owing to high capital/ operational costs, resulting in the generation of chemical sludge waste that must be treated before disposal as it poses hazards and pollution risks to the atmosphere[5]. Adsorption process involves use of low-cost, naturally occurring and readily available agricultural/ animal waste materials as adsorbents[6]. In this current study, *Prosopis juliflora* bark an agro-waste has been investigated for the remediation of industrial leachates containing Pb(II) and Cd(II) ion through adsorption process.

Materials and Methods

Prosopis juliflora bark (PJB) was collected from various localities in Coimbatore, washed thoroughly with distilled water to remove impurities, air-dried and sieved into different particle sizes viz., 22 BSS (0.71 mm), 36 BSS (0.42 mm), 52 BSS (0.30 mm), 72 BSS (0.21 mm) and 85 BSS (0.18 mm) using standard Scientific Test Molecular Sieves. In order to enhance the active sites and metal sorption capacity, the sieved materials were treated with 0.1 N HCl for 3 hours, washed several times to attain pH 7 with doubly distilled water, dried, stored in airtight containers for further experiments and referred to as TPJB. Stock solutions of Lead and Cadmium (1000 mg/ L) were prepared by dissolving Lead nitrate and Cadmium acetate salt, in 1000 ml of doubly distilled water. Working standards were prepared by progressive dilution of stock copper and cadmium solutions. The influence of various parameters like particle size (0.18mm-0.71mm), sorbent dosage (100mg- 500mg), initial concentration (50, 100, 150 and 200 mg/ L), agitation time interval (5-30 minutes) and pH (3, 5, 7, 9 and 11) were assessed by Batch Equilibration experiments at room temperature to optimize the favorable conditions for maximum uptake of the selected sorbate species. pH measurements were performed with a controlled pH analyzer (LABTRONICS). The agitated samples were filtered and the initial/residual concentrations of Pb(II) and Cd(II) were analyzed using Atomic Absorption Spectrophotometer (AA- 6200, Shimadzu Make).

Surface characteristic Studies

The treated and metal loaded TPJB were subjected to spectral analyses (within the range of 400-4000 cm-1) to determine the functional groups present in TPJB using *Shimadzu Infrared Spectrophotometer*. Morphology and elemental constitutions of the unloaded and loaded adsorbent material were identified using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDAX)(*JEOL JFM- 6390*).

RESULTS AND DISCUSSION

FTIR Spectral analysis

The possibilities of functional groups present in TPJB involving sorption of Pb(II) and Cd(II) ions determined using FT-IR Spectroscopic studies are depicted in fig 1a – 1d. Fig 1(b) shows the appearance of peaks at 3335.79 cm^{-1} and 1746.62 cm^{-1} corresponding to O-H and C=O. The disappearance of O-H band at 3335.79 cm^{-1} in fig 1c and 1d indicate the probable formation of metal oxygen bond during sorption.

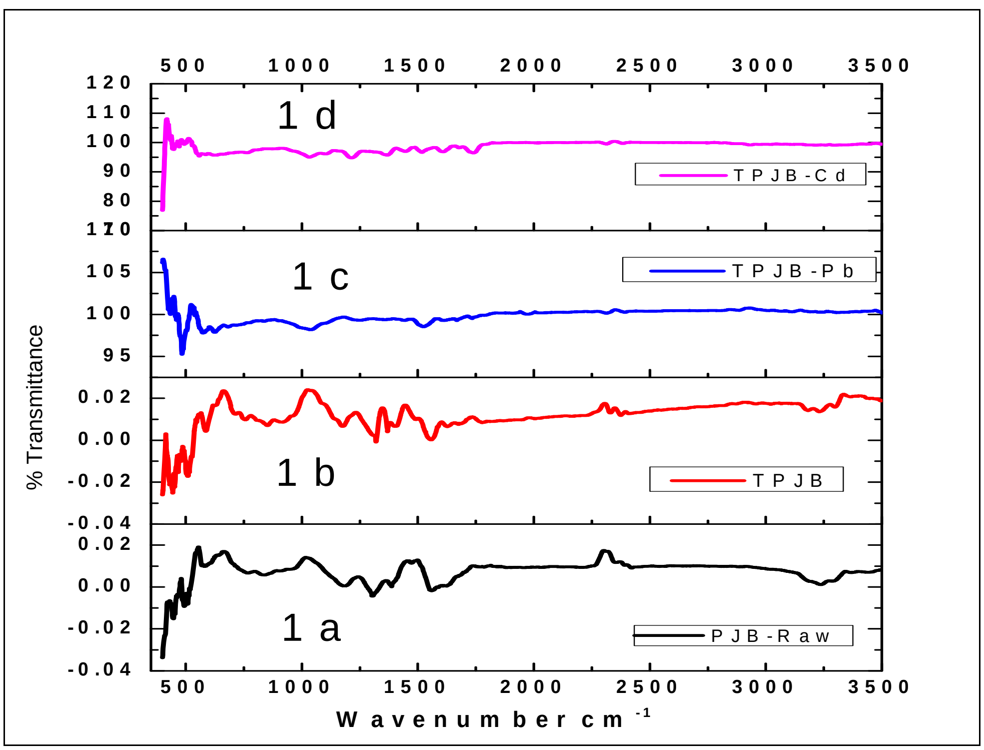

Fig 1a: Raw PJB, Fig 1b: unloaded PJB, Fig 1c: Pb(II) loaded TPJB and Fig 1d: Cd(II) loaded TPJB

Surface Morphology SEM images of unloaded and metal laden TPJB have been depicted in figs 2a, 2b & 2c. Fig 2a registers a high porous morphology and a coarse surface texture with different shapes and sizes. The morphological changes as obvious from fig 2b & 2c suggest that effective sorption of Pb(II) and Cd(II) had occurred on the sorbent surface.

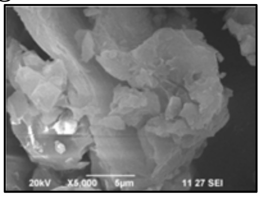

Fig 2a: Raw PJB

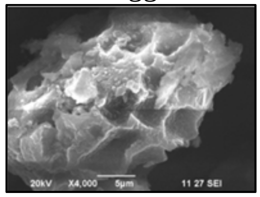

Fig 2b: unloaded TPJB

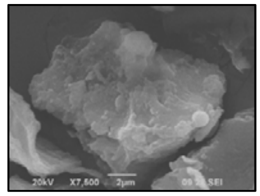

Fig 2c: Pb(II) loaded TPJB

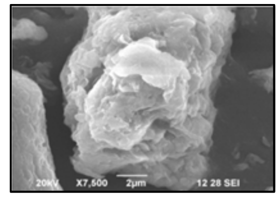

Fig 2d: Cd(II) loaded TPJB

EDAX Analysis

The recorded EDAX spectra registers the elemental constitution qualitatively where percentage of O, C, Ca and Cl are 47.13, 52.2, 0.58 and 0.09 respectively in TPJB. These have been reported as the principle elements of the adsorbent. The appearance of new peak in figure 3c and 3d, confirm the presence of Pb(II) and Cd(II) in the loaded counterparts.

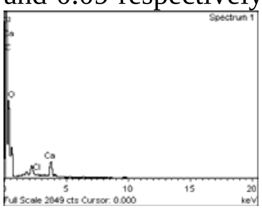

Fig 3a: Raw PJB

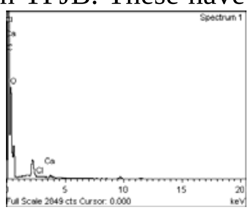

Fig 3b: unloaded TPJB

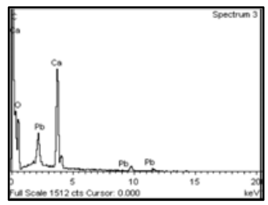

Fig 3c: Pb(II) loaded TPJB

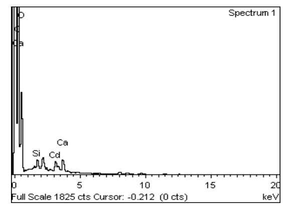

Fig 3d: Cd(II) loaded TPJB

Effects of Particle Size

Particle size plays a vital role in determination of metal sequestering capacity of TPJB from aqueous solutions. Both the systems registered a maximum sorption capacity (mg/g) against smallest the particle size of 0.18mm amongst the chosen sizes (fig 4). This can be explained by the fact that relatively smaller particle size yields large surface area[7].

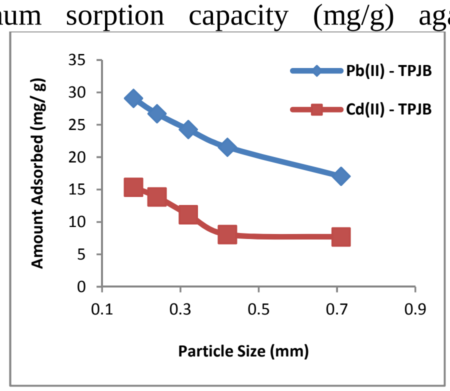

Fig 4: Effects of Particle Size

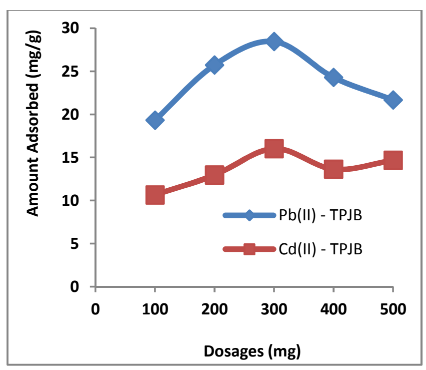

Fig 5: Effects of Dosage

Effects of Dosage

Removal of Pb(II) and Cd(II) ions were found to be less at lower doses, but exponentially increased and reached an equilibrium point at 300 mg (figs 5). The declination in the metal uptake above equilibrium state is due to the partial aggregation among the active sites at higher doses and lack of binding site at lower doses[8] are responsible for the retardation of metal ions sorption onto the TPJB.

Effects of Initial Concentration and Agitation Time

Pb(II) and Cd(II) ion removal as a function of initial metal ion concentration and agitation time are given in fig 6 and 7. An inclination in the adsorption curve from 50 - 100 mg/ L is obvious in fig 6 which may be due to abundant availability of active sites on the sorbent surface to trap these metal ions and the declining curves indicates the saturation of the sorption sites for complexation of metal ions at higher concentration[9]. The maximum removal observed for Pb(II) -TPJB and Cd(II) -TPJB are

93% (15 min) and 81% (20 min) respectively. The highest uptake value of Pb(II) corresponds to the lower hydrated ionic radius of Pb(II) ions (2.61 Å), compared with Cd(II) (2.75 Å), also higher charge density favours attractive electrostatic interactions between the TPJB and Pb(II) ions[10].

Effects of pH

pH dependance for maximum removal of metal ions onto TPJB was studied at varying pH environments viz., 3-11. It is evident from Fig. 8 that maxima adsorption had occurred at pH 5 for Pb(II) and pH 7 in case of Cd(II) ions as indicated by the inverted parabolic curves. The reduced sorption rate at highly acidic and alkaline pH ranges may be attributed to the protonation of the sorption sites and preferential hydroxyl complex formation of the metal ion[11].

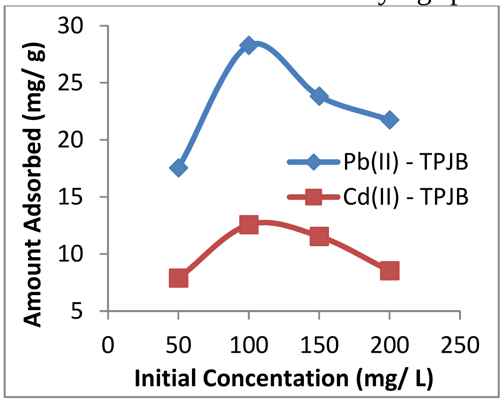

Fig 6: Effects of Initial Concentration

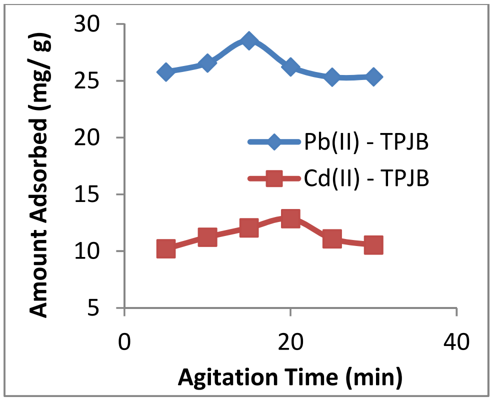

Fig 7: Effects of Agitation Time

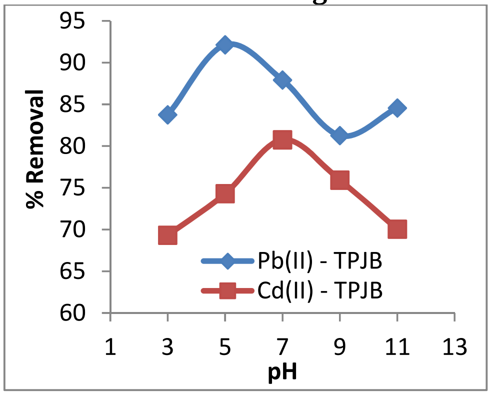

Fig 8: Effects of pH

Isotherm studies

The equilibrium data were modeled using Langmuir, Freundlich isotherms and Table 1, lists out the isothermal constants with correlation coefficients.

The relation between sorbent and sorbate is provided by Langmuir constant *b*.[10] Higher q_m, b and R^2 value were observed for Pb(II)-TPJB system than Cd(II)-TPJB system (fig 9).

Freundlich isotherm [fig 10] presents lower correlation coefficient (R^2) values when compared to Langmuir values. K_f is an indicator of the adsorption capacity and 1/n is the adsorption intensity. The magnitude of the exponent 1/n, shows the favorability of adsorption.

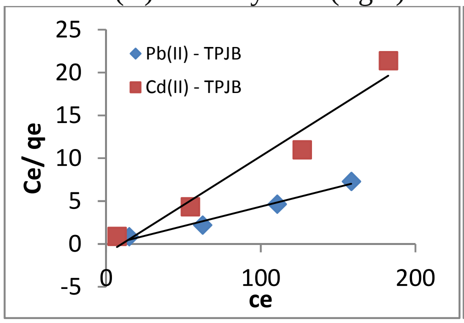

Fig 9: Langmuir Isotherm

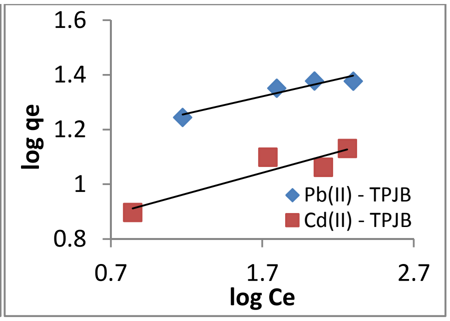

Fig 10: Freundlich Isotherm

Table 1: Isothermal Constants

System	Langmuir			Freundlich		
	Q_m	b	R^2	n	K_f	R^2
Pb(II) - TPJB	27.4725	5.1621	0.9818	7.9428	12.8026	0.9178
Cd(II) - TPJB	11.0011	12.7304	0.9574	0.7833	6.0715	0.8596

Conclusion

Tree barks of *Prosopis juliflora* was an effective biosorbent for the adsorption of Pb(II) and Cd(II) ions from aqueous solutions. The FTIR spectra showed that O-H functional groups are responsible binding sites of the metal ions in both the systems. SEM and EDAX analyses of unloaded / loaded material, registered a significant changes in porosity structure and appearance of Pb(II) and Cd(II) peaks supporting the adsorption positively. Batch equilibration experiments revealed maximum percentage removal of 92% of Pb(II) – TPJB and 81% of Cd(II) – TPJB systems under the optimized conditions of 0.18 mm particle size, 300 mg dosage, 100 mg/ L initial concentration at 15 min (pH 5) and 20 mins (pH 7) time intervals respectively. The isothermal data favoured the monolayer adsorption of Pb(II) and Cd(II) ions. The concluding remarks promises TPJB as potential adsorbent for possible remediation of wastewater contaminated with lead and cadmium ions.

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