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Biosorption efficiency of tea residue for analysis of cadmium and lead ions using open circuit potential for real time measurement

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Abstract

The present paper reports the biosorption efficiency of tea residue (TR) for extermination of Pd^{+2} and Cd^{+2} ions from aqueous system using potentiometry as analytical tool. A three electrode cell setup with metal-coated gold (Au) electrode and platinum (Pt) electrode were utilized in form of working electrode for Pb^{+2} and Cd^{+2} deposition, respectively. Open circuit potential (OCP)values of metal ion concentration were observed which decreased for both heavy metals with addition of TR. Fourier transform infra-red (FTIR) spectroscopy showed the involvement of OH, C=O and C-O functional groups in the biosorbent. Scanning Electron Microscopy (SEM) analysis was carried out to study morphological features and showed the porous surface associated with biosorbent. The biosorption efficiency was analyzed to be 126 $mg.g^{-1}$ for Pb^{+2} and 60.52 $mg.g^{-1}$ for Cd^{+2}. TR was found to be a potential biosorbent for removal of Pd^{+2} and Cd^{+2}ions from aqueous solution. OCP built method offers a green approach which is uncomplicated for real time analysis of biosorption efficiency.

Keywords: Tea residue, Lead, Cadmium, Open Circuit Potential, Biosorption.

Introduction

Water pollution originating due to presence of heavy metals, released from industries is pervasive in developing nations such as India[1]. Heavy metal pollution has become a considerable threat globally due to their non-biodegradable and persistent character[2]. Heavy metals like Lead (Pb) and Cadmium (Cd) can have hazardous effects on humans and plants even at lower concentrations. In accordance with World health organizations (WHO), the agreeable limits of Pb (II) and Cd (II) in drinking water are 0.01 and 0.03 ppm, respectively. Thus, it is exigent to minimize the concentration of heavy metal ions in water. Many techniques have been employed for the same such as electrodialysis, coagulation and flocculation, ion-exchange method, membrane separation, reverse osmosis, adsorption etc[3].

Adsorption stands out as a promising technique owing to its simplicity, ease of operation, high efficiency and economic benefits[4,5]. Heavy metals are removed when they come in association with ion exchange resins or activated carbons but these methods are marked with high cost and unavailability to poverty stricken areas. Hence, there is a need to look for alternative low cost adsorbent materials. Thus, use of inexpensive biomass material has gained an insight for heavy metal adsorption[6]. Many low cost adsorbent materials such as clay, sewage sludge, coal fly ash; agricultural wastes/biomasses have been used in eviction of heavy metals from water[7,8].

After water, tea (*Camellia sinensis*) is mostly consumed in the world as a beverage. After the beverage has been brewed, tea wastes need to be disposed off as they are considered as unused resource and pose disposal problems. It is thus important to look for strategies which utilize these resources as value added products or as an energy source. The cell wall of tea residue (TR) comprises of cellulose, carbohydrates and lignin which are associated with hydroxyl functional groups and hence about one-third of TR should have potential as metal scavengers from aqueous solution[9,10]. It has been shown that TR can be effectively used for removal of metal ions with an efficiency of about 100% by selecting the adsorbent amount precisely[11].

Thus, use of such biosorbents has led to a greener approach for remediation of heavy metal pollution. Biosorption is a low cost, effective and environmental friendly technology. Relatively, batch mode adsorption experiments, for optimizing biosorption efficiencies of various biomasses, are found to be tedious. This limitation can be overcome by using potentiometry based adsorption using OCP. This method offers advantage of being cheap at cost, improved efficiency; unsubstantially time consuming and minimum quantity of sludge is generated[12].

Open Circuit Potential is that potential at the working sensor while limited current is supplied externally to the circuit[13]. Biosorption efficiency of plant biomass can be monitored by measuring OCP of metal ions in equilibrium, during and after addition of biosorbent. After biosorbent addition, an appreciable decrease is observed due t reduction of metal ions concentration and uptake of metal ions[14,15].

Present piece of work is determined to use TR as an adsorbent material to remove or minimize the concentration of heavy metal ions such as Pb^{+2} and Cd^{+2} in real time experimental work, leading to reinforcement of a new analytical method.

Materials and methods

Chemical and reagents: The reagents used in this experiment were of analytical grade quality. $NaClO_4$, Pb $(NO_3)_2$ and $Cd(NO_3)_2.4H_2O$ were bought from Qualigens. All the solutions were prepared using Milli-Q water from ELGA Purelab Options Q. Stock solutions were diluted to prepare the working solutions. All the solutions were deoxygenated by passing nitrogen gas into the solutions before the experiments.

Apparatus: Potentiometric measurements were done using an Autolab potentiostat (PGSTAT-302 N) which operated using the software NOVA 2.1. A three electrode system was used at 25°C ± 1°C. An Ag/AgCl as reference electrode, platinum as counter electrode and a platinum wire as working electrode for Cadmium (Cd) and a gold wire as working electrode for Lead (Pb) (Figure-1).

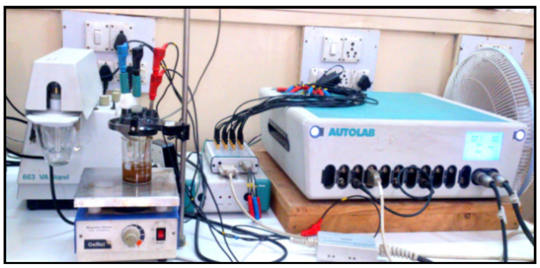

Figure-1: Autolab potentiostat PGSTAT-302N with a three electrode setup.

Preparation of biosorbent: Tea residue was procured from a local tea vendor in Dayalbagh, Agra. It was washed repeatedly to remove all the coloring components till no color was observed spectrophotometrically. Afterwards, material was oven dried for 24 hours at 60^o C. Dried material was grounded and sieved to a particle size less than 150µm (Figure-2).

Figure-2: Prepared adsorbent material (TR); particle size: <150µm

Characterization of biosorbent: Fourier Transform Infra-red spectroscopy (FTIR) was done for functional group investigation using Cary 630 FTIR spectrophotometer (Agilent Technologies). Surface morphology was studied using Scanning Electron Microscopy (SEM) LEO 430, Cambridge (U.K.).

Procedure: Pb $(NO_3)_2$ (1mM) and $Cd(NO_3)_2.4H_2O$ (5mM) were prepared in 0.1 M $NaClO_4$. Linear seep voltammetry (LSV) was used for electrodeposition of metal ions onto the surface of working electrode. For depositing Pb^{+2} ions a linear sweep was applied from 0 to -0.8 V while for Cd^{+2} ions linear sweep was applied between 0 to -1.5 V at 100 mVS^{-1}. The working electrodes were Pb or Cd electrodeposited on gold and platinum respectively. Then, electrodes were immersed in the working solution followed by OCP values measurement which was taken between the working and reference electrode. After achieving stability, TR powder was added subsequent change in OCP value was determined. An excruciating decrement was observed in the OCP value which further enhanced to reach a stable value. This was followed by a second addition of TR powder and OCP value was determined. OCP versus time plot was used to analyze changes in the OCP value on increasing the amount of TR powder.

Theory: OCP is defined as the potential of working sensor respective to reference sensor while no current is allowed to flow through the cell. For quantification of metal in solution, the difference between the OCP value prior to addition and after the addition of biomass is measured.

$$\Delta OCP = 0.0296 \log \frac{[M^{2+}]final}{[M^{2+}]initial} \quad (1)$$

As initial metal ion concentration is known, final concentration can be determined when biomass is added. The amount of metal ion that binds to biomass was calculated using volume of solution used and mass of biomass.

Results and discussion

Fourier Transform Infra-red spectroscopy (FTIR): The interaction of Pb (II) and Cd (II) with the biomass can be explained through FTIR spectrum (Figure-3). The peak at 3430.16 cm^{-1} indicates presence of free O-H functional group of phenols and polyphenols in cellulose and lignin. Peak at 2924.958 cm^{-1} indicates C-H stretching mode which shows aliphatic nature of adsorbent. Peaks around 1647.96 cm^{-1} and 1077.518 cm^{-1} correspond to C=O group and C-O stretching respectively. The bands around 1636.29 cm^{-1} to 1496.23 $^{cm-1}$ corresponds to C=C in aromatic rings. A shift in peak has been observed from 3430.16 cm^{-1} to 3432.46 cm^{-1} and 1647.96 cm^{-1} to 1649.89 cm^{-1} in Pb treated biomass. Shift from 3430.16 cm^{-1} to 3435.21 cm^{-1} and from 1647.96 cm^{-1} to 1648.2 cm^{-1} was observed for Cd treated biomass. The shifting occurred as a result of binding of metal ions (positively charged) with the functional groups (negatively charged).

Scanning electron microscopy (SEM): SEM micrographs of TR before and after metal ion adsorption are shown in Figure-4. The SEM micrograph of TR exhibits rough surface with pores and fibrous structures. A rough is beneficial for adsorption of metal ions[16]. Pb (II) and Cd (II) treated TR shows that surface is covered with metal ions making it more uneven thus indicating adsorption of metal ions onto the surface of biosorbent.

Electrode position: LSV was applied for Pb(II) and Cd(II) deposition on gold (Au) and platinum (Pt) electrode respectively. The cathodic peak for Pb(II) appeared at -6.5V and that for Cd(II) at -1V corresponding to reduction of Pb^{+2} and Cd^{+2} and accumulation onto electrode surface (Figure-5).

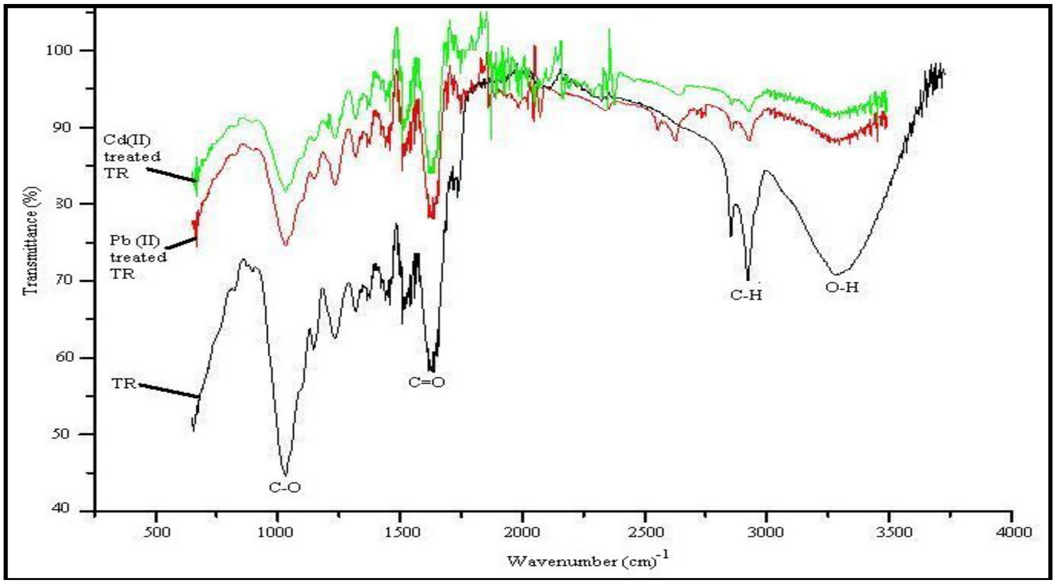

Figure-3: FTIR spectra of TR, Pb (II) and Cd (II) treated TR.

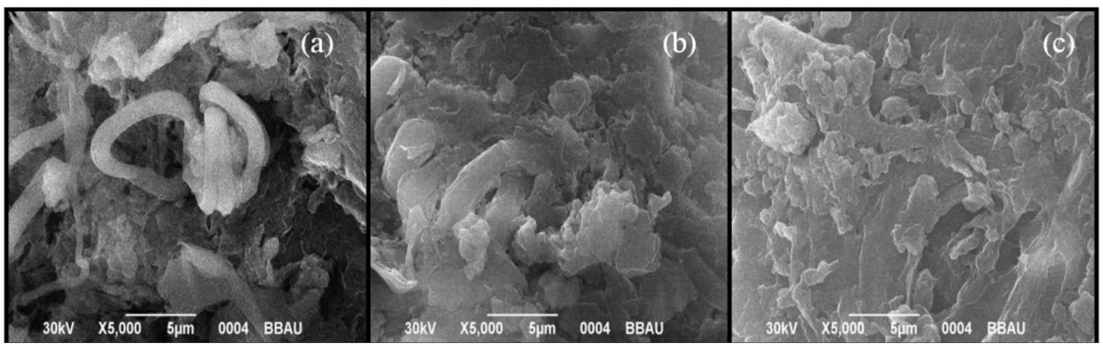

Figure-4: SEM micrographs of TR (a) Pb (II) treated TR (b) and Cd (II) treated TR (c).

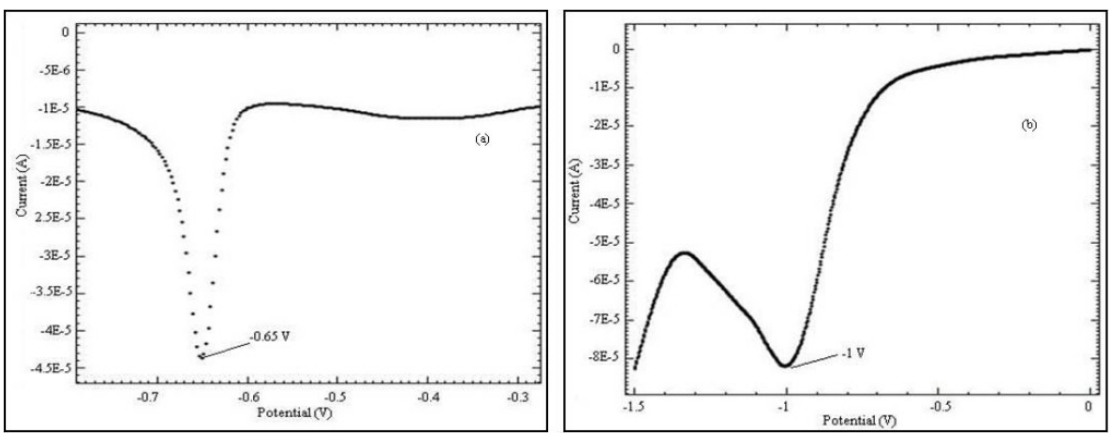

Figure-5: Linear sweep voltammogram for deposition of metal ions: (a) Pb (II) and (b) Cd (II).

Determination of OCP values: Following the accumulation step, metal ions solution was shuffled with working solution and metal ion-coated working electrodes were placed into it along with the reference electrode. All the OCP values were determined and a plot of OCP versus time was taken (Figure-6). OCP values were observed to increase initially and then get stabilized further. A decrease in OCP value is observed on addition of biomass. The amount of biomass added for both Pb(II) and Cd(II) was 0.1g during 1st and 2nd additions. The pH of solution was maintained at 5 using acetate buffer. The sorption efficiency was calculated using Equation 1 and found to be 126 mg/g for Pb(II) and 60.52 mg/g for Cd(II).

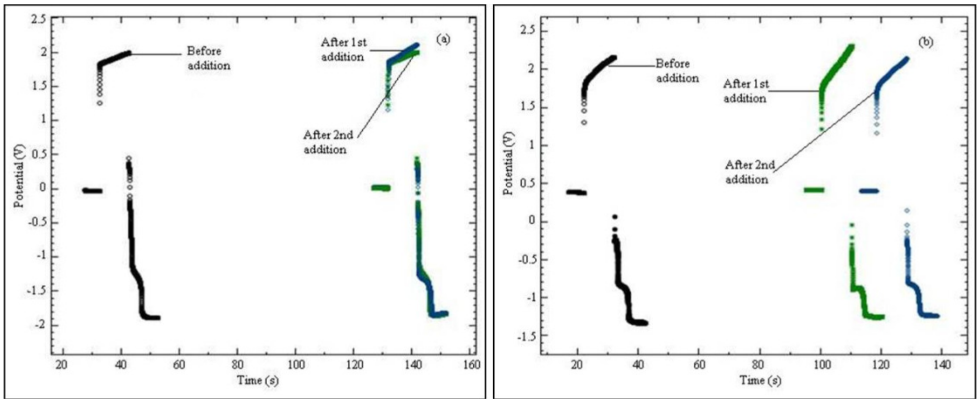

Figure-6: Variation of OCP value with time on biomass addition at pH 5 for Pb(II) biosorption (a) and Cd(II) biosorption (b).

Conclusion

Present work describes a distinct analytical method for analyzing the potential of tea residue to remove Pb^{+2} and Cd^{+2} from aqueous solutions. The results clearly indicate that tea residue is an efficient biosorbent material for Pb(II) and Cd(II) ions removal with maximum efficiency of 126 mg/g and 60.52 mg/g respectively. FTIR results show the involvement of hydroxyl and carbonyl groups during sorption process. Surface porosity and adsorption of metal ions to the surface of biosorbent was indicated by SEM. OCP measurement technique serves as a promising analytical tool for measuring the sorption efficiencies in real time situations. Utilization of tea residue along with OCP technique is an environmental friendly approach for combating heavy metal pollution.

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