Nepal Journal of Science and Technology Vol. 13, No. 2 (2012) 109-114

Adsorptive Removal of Toxic Metal from Aqueous Solution by Using a Biowaste -Used Tea Leaves

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Abstract

In the present work an efficient and cost-effective biosorbent was prepared by chemical modification of tealeaves. Amine-functional group was introduced on the surface of adsorbent using dimethylamine. The adsorbent was characterized by SEM, FTIR and elemental analysis. The adsorption capacity of the adsorbent for Cd (II) was determined as the function of pH of the solution, concentration of metal ions and contact time. The maximum adsorption was found to be 77 mg/g at pH 6.

Key words: amination, biosorbent, cadmium, Langmuir isotherm

Introduction

Environmental pollution by heavy metals is of major concern, because of their toxicity and bio-accumulating tendency. They threat human life and the environment (Nurchi *et al*. 2008). Cadmium is a non-essential and non-beneficial element to plants and animals. It is one of the priority pollutant and included in 'the big three' (most toxic) heavy metals (Volesky *et al*. 1995). The toxicity of cadmium in human health includes disfuntioning of kidney, hepatic damage, hypertension and itai-itai disease (Igwe *et al*. 2006).

To remove heavy metals from wastewater various conventional methods like chemical precipitation, filtration, flocculation, reverse osmosis, coagulation, ion exchange, ultra filtration and electrochemical deposition were used (Babel *et al*. 2003). But these conventional methods become non-efficient and non-feasible when concentration of the metal is in trace amount ranging from 1-100 mg/l. In such cases adsorption process using agricultural waste as biosorbent can be used as an attractive alternative for wastewater treatment (Ayyappan *et al.* 2005).

Biosorbents are prepared from naturally abundant waste biomasses which are economically acceptable. They have high metal adsorption capacity and can be reused after desorption of metal ions. Many researchers have been investigating new biosorbents like sugarcane bagasse (Homagai *et al.* 2011), orange waste (Biswas *et al.* 2007), saw dust (Basso *et al.* 2002), olive stone (Blazquez *et al*. 2005), sea weeds (Ghimire *et al.* 2007), wheat straw (Chen *et al*. 2010) and chitin (Jeon *et al*. 2004) for the removal of heavy metals from wastewater. In the present study used tealeaves have been used as a biowaste for the removal of Cd (II) from aqueous solution. The biosorbent was aminated to introduce amino-functional group on the surface of the adsorbent. The effectiveness of adsorbent was studied by determining the maximum adsorption capacity using batch method.

Methodology

Fifty grams of used tealeaves was washed with hot distilled water till the filtrate became clear. The biowaste was dried in an oven at 70^{o}C. The dried mass was treated with concentrated sulphuric acid, which dissolved the soluble substances and expossd the surface of biopolymer for further treatment. This acid treated biowaste was washed thoroughly with distilled water till the filtrate became neutral and dried in an oven. The charred biowaste was mixed with thionyl chloride ($SOCl_2$) in presence of pyridine at 0^{o}C. The mixture was heated at 70^{o}C for 2 hrs and cooled. The remaining thionyl chloride was decomposed with ice. The sample was filtered and washed with distilled water followed by propanol and dried. The chlorinated sample was then aminated by dimethylamine in presence of dimethylsulphoxide (DMSO) and sodium carbonate at 70°C for 6 hrs. The mixture was cooled, filtered and washed with 0.1 M HCl followed by distilled water. Finally the adsorbent was washed with propanol and dried in an oven at 70°C for 24 hrs. The aminated adsorbent is called aminated tealeaves (ATL).

The 1000 mg/l stock solution of Cd (II) was prepared by dissolving calculated amount of Cadmium nitrate [$Cd(NO_3)_2.4H_2O$] in 0.1 M HNO_3. The stock solution was diluted to required dilution to prepare working solution of different concentration. The pH of experimental solutions were maintained using nitric acid and sodium hydroxide and [2-4-(2-hydroxymethyl)-1-piperazinyl] ethanesulphonic acid [HEPES] was used as buffer. Analytical grade reagents [AR] were used for all experimental works.

The adsorption experiments were studied by using batch sorption experiments. All the experiments were performed at 25°C and 150 rpm on a mechanical shaker with 25 mg of adsorbent in 50 ml conical flask containing 20 ml of Cd (II) solution. The effect of pH of the solution, initial concentration and contact time were studied. After adsorption, the mixture was filtered through Whatman filter paper (no. 40). The concentration of Cd (II) in solution before and after equilibrium was determined by atomic absorption spectrophotometer (AAS) using air acetylene flame.

The adsorption efficiency A% of the adsorbent was calculated by using equation (1)

$$A\% = \frac{C_i - C_e}{C_i} \text{ X } 100 \qquad (1)$$

where C_i and C_e are concentration of metal ions in mg/l before and after adsorption experiments.The amount of metal adsorbed i.e. sorption capacity q_e (mg/g) was computed by using equation (2)

$$q = \frac{C_i - C_e}{W} \text{ X V} \qquad (2)$$

where V is volume of metal solution (l) and W is weight of adsorbent (g).

Results and Discussion

Characterization

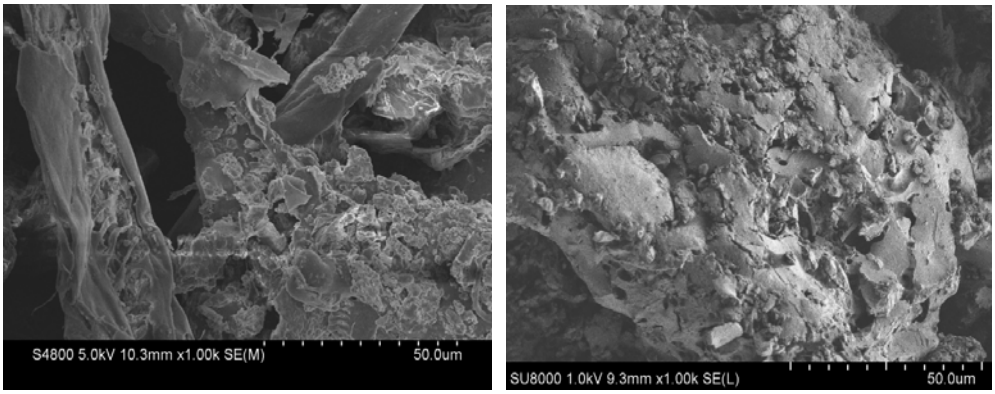
To enhance the adsorption capacity of the biosorbent, it was chemically modified with dimethylamine. It is supposed that the alcoholic and phenolic OH groups present in cellulose, hemicellulose and lignin of the biosorbent are substituted with amino-functional groups. The amino-functional groups have been found to be more effective chelating group for adsorption of metals from aqueous solution. The N atom of the functional group has greater tendency to donate a lone pair of electrons for sharing with metal ions to form a metal complex. Hence, there has been considerable interest for introduction of N-functional group on the surface of adsorbent to enhance the adsorption capacity. In this study amino-functional group was introduced on the surface of the bioadsorbent by using dimethylamine. The aminated biosorbent was characterized by scanning electron microscopy (SEM), fourior transform infrared spectroscopy (FTIR) and elemental analysis.

Scanning electron microscopy

The scanning electron microscopic images were used to examine the surface morphologies of waste tealeaves before and after chemical modification (Sankaramakrishnan *et al*. 2006). The images are given in Fig. 1. Initially the surface of biosorbent is smooth with uniform microporous structure which becomes rough after amination indicating the modification of the adsorbent.

Fouir-transform infrared spectroscopy

In FTIR analysis, each specific chemical bond often shows a unique energy absorption band and it has been used as a useful tool to identify the presence of certain functional groups on the surface of the biosorbent (Shriner *et al.* 1998). The FTIR spectra of TL and ATL are shown in Fig. 2. The spectra are complex due to numerous different types of functional groups on the surface of adsorbent. In the spectrum of TL, the peaks can be assigned as follows, 3388 cm^{-1} was due to OH stretching, 2924 cm^{-1} due to CH stretching in CH, CH_2 and CH_3 groups, 1646 cm^{-1} due to C=O stretching in carbonyl group and 1078 cm^{-1} due to C-O stretching. After chemical modification the spectrum exhibits some significant changes. The broad band ranging from about 3118 to 3650 cm^{-1} corresponds to the combination of stretching vibration bands of both OH and NH groups suggesting that N-functional groups are introduced on the surface of the biosorbent. The peaks at 1450 cm^{-1} and 1033 cm^{-1} are due to the C-H bending and C-N stretching, respectively. The increase in percentage of nitrogen in elemental analysis of ATL 5.56% than in TL 1.03% also further supports the introduction of amine functional groups on the surface of biosorbent after chemical modification.



1(a) 1(b)

Fig. 1. SEM images of tealeaves (TL) and aminated tealeaves (ATL)

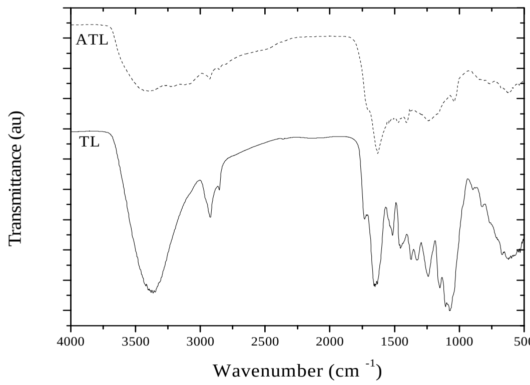


Fig. 2. FTIR spectra of tealeaves (TL) and aminated tealeaves (ATL)

Effect of pH

The adsorptive removal of metal ions from aqueous solution is dependent on the pH of the solution as it affects the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. To study the effect of pH on the Cd (II) removal efficiency the pH of the solution was varied from 1-6. As shown in Fig. 3, adsorption increases with increase of pH and maximum removal of Cd (II) was observed at pH 6. On further increase in pH precipitation occured. At low pH, protons would compete for the binding sites with metal ions. The protonation of adsorbent surface tends to decrease the metal sorption. At higher pH concentration of protons decreases and the surface of the adsorbent became negative which increases the adsorption of metal ions.The solubility of metal ions also decrease at higher pH facilitating the adsorption. The further increase of pH results in precipitation of metal ions as hydroxides.

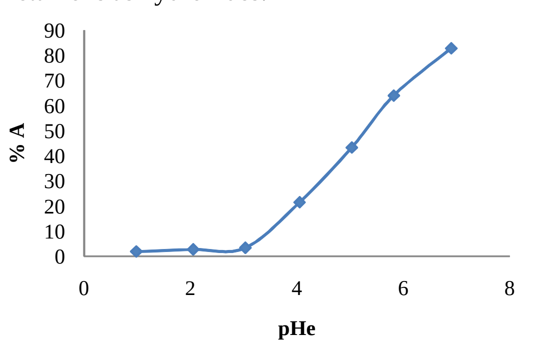


Fig. 3. Effect of pH on adsorption of Cd (II) onto ATL

Effect of initial concentration

The study of adsorption isotherm indicates the adsorption capacity of the adsorbent at experimental condition. Fig. 4. shows the plot for the adsorption isotherm. In the plot, the adsorption of metal ions increases initially with increase in equilibrium metal concentration. The uptake of metal ions is eventually limited by the occupied active sites and results in a plateau. It suggests that metal ions are adsorbed according to Langmuir model. The linear form of Langmuir isotherm is given by equation (3)

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (3)$$

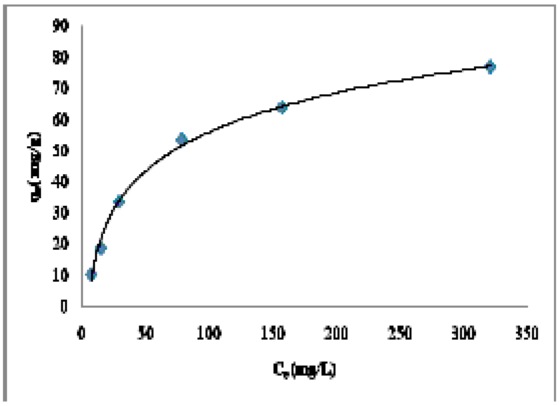


Fig. 4. The adsorption isotherm of Cd (II) onto ATL

where q_e is amount adsorbed (mg/g), C_e is equilibrium concentration of metal ions (mg/l) and q_m and b are Langmuir constants. The linear plot of C_e/q_e versus C_e as shown in Fig.5. suggests the applicability of Langmuir adsorption model and indicates the formation of monolayer coverage of metal ions on the surface of adsorbent.

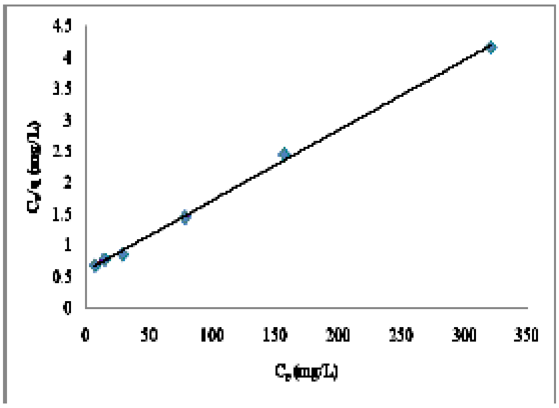


Fig. 5. Langmuir isotherm plot for the adsorption of Cd (II) onto ATL

Effect of contact time - kinetics of adsorption

Adsorption kinetics is studied to evaluate the efficiency of adsorption. The effect of contact time on adsorption of Cd (II) onto ATL is shown in Fig. 6. The plot consists of initial rapid adsorption phase and a slower phase where equilibrium uptake was achieved. The initial high rate of adsorption of metal ions is due to free active binding sites on the surface of the adsorbent. As the number of available sites decrease the rate of adsorption of metal ions also decrease.

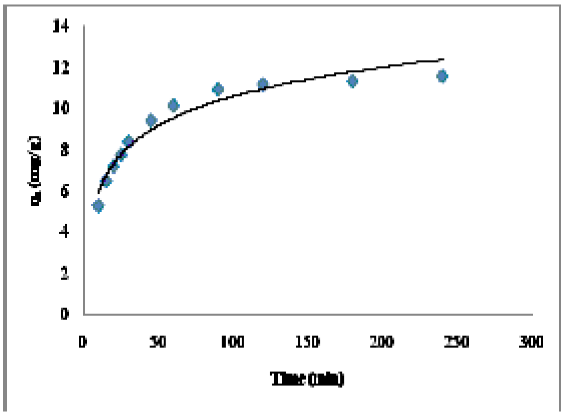


Fig. 6. Adsorption kinetics for Cd (II) onto ATL

To describe the kinetics of adsorption pseudo-second order kinetic model is applied (Ho *et al.* 1999). It is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where q_t is the amount adsorbed at time t (min) and k_2 (g/mg/min) is the rate constant of pseudo-second order kinetics of adsorption. The plot of t/q_t versus t is given in Fig. 7.

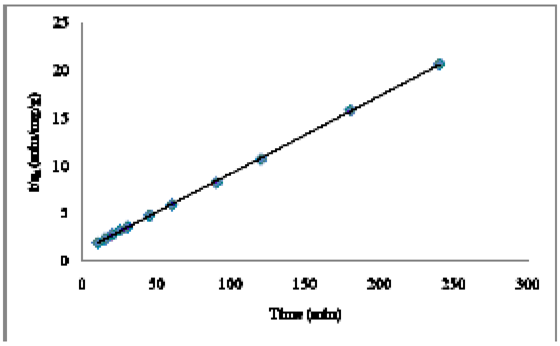


Fig. 7. Pseudo-second order kinetics Cd (II) onto ATL

The plot is a straight line with high correlation coefficient value. It indicates that pseudo-second order kinetic model can be applied for adsorption of Cd (II) onto ATL and also indicates the chemisorption of the metal ion.

In present work N-functional group was successfully introduced onto the surface of biosorbent. The adsorbent was characterized with SEM, FTIR and elemental analysis. The adsorption capacity was studied as the function of pH of the solution, concentration of the solution and contact time. The maximum loading capacity for Cd (II) was found to be 77 mg/g. Hence, the aminated tealeaves can be used as an efficient biosorbent for removal of Cd (II) from wastewater.

Acknowledgements

One of the authors, B. Shrestha, gratefully acknowledges Nepal Academy of Science and Technology (NAST), Nepal, for providing Ph.D. fellowship to carry out this research work.

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