Kush - A Potential Biosorbent in the removal of Cd (II) and Zn (II) from aqueous solution

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Abstract

The industrial discharge of heavy metals into waters' course is one of the major pollution problems affecting water quality. Therefore, they must be removed prior to their discharge into waste streams. An efficient and low-cost bioadsorbent has been investigated from Desmostachya bipinnata (Kush) by charring with concentrated sulphuric acid and functionalized with dimethylamine.It was characterised by SEM, FTIR and elemental analysis. The effect of pH, initial concentration and contact time of the metal solution was monitered by batch method. The maximum adsorption capacities were determined for Cd and Zn at their optimum pH 6. The equilibrium data were analysed using Langmuir and Freundlich isotherm models. Langmuir isotherm model fitted well and the rate of adsorption followed the pseudo second order kinetic equation.

Keywords: *Pollution, low-cost bioadsorbent, functionalization, elemental analysis, adsorption isotherm.*

Introduction

Excessive release of heavy metals into the water bodies and environment due to industrial as well as human activities is a matter of global concern affecting water quality [1, 2, 3]. Heavy metals like Cd(II). Cr(III), Cu(II), Hg(II), Zn(II) are discharged from numbers of industries like electroplating, dyes, textiles, tanneries, oil refineries, photpgraphy, battery, smelters, welding, pesticides and printing.[3] Unlike organic wastes, heavy metals are non-biodegradable and their harmful effects in aquatic environment includes accumulation in living species and magnification throughout the food chain [4,5,6].Therefore, they must be removed before descharge into waste streams. Many research works are in progress for the development of the cheaper and efficient treatment techniques to replace conventional treatment techniques such as ion exchange, membrane separation, and synthetic ion exchange resins. On the other hand, carbon adsorption is costly [7, 8, 9]. Biosorption is a low cost alternative method for the removal of heavy metals with very little amount of waste sludge as well as high degree of eficiency in decontaminating very dilute effulents [10,11,12,13]. The most commonly used agricultural wastes are renewable, cheap and their handling involves no additional risk [19, 20, 21]. In the present study, the

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biomass of Kush plant is used as a biosorbent in the removal of heavy metals from aqueous solution. The aim of this study is to investigate the adsorption capacity and the kinetics of the Cd (II) and Zn (II) ions onto the Kush plant.

Experimental Methods

Sample preparation

The whole plant of Kush was used as biosorbent in this study. It was dried and cut into small pieces and washed with water and dried in sun and finally in an oven at 70 ^{0}C for 24 h. The oven dried sample was grounded into fine powder using a grinding mechine. It was sieved through 212 micro meter siever. This sample is known as Raw Kush Powder (RKP).

About 100g of RKP was charred with concentrated sulphuric acid and left overnight.The sample was throughly washed with distilled water till neutrality and dried in air followed by oven dry at 70^{0}C for 24 h. The charred Kush powder was treated with thionyl chloride in ice cold condition in presence of pyridine and heated on a water bath at 70 ^{0}C for one and half hour. The mixture was cooled and washed with distilled water till neutral pH, then finally with propanol and left to air dry.This resulting biomaterial was taken in three necked round bottom flask along with dimethyl sulphoxide (DMSO), sodium carbonate and dimethylamine.The mixture was heated for 48 h at 70^{0}C, cooled, filtered and washed with 0.1 M hydrochloric acid, then with water till neutral pH and finally with propanol. The biomaterial was air-dried and then oven dried for 24 h at 70^{0}C and is rererred as Aminated Kush Powder (AKP).

Preparation of solutions

1000 mg/L standard stock solution of Cd (II) and Zn (II) metal ions were prepared from their corresponding nitrate and sulphate salts by dissolving in deionised water. The standard stock solution was further diluted with 0.1M nitric acid in order to prepare the working solutions of desired concentration. 0.1M 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethane sulphonic acid (HEPES) was added in all working solutions as buffering agent [14, 15, 16].

Effect of pH

For pH study, 50 mg/L of Cd (II) and Zn (II) metal ions were taken and their pH were mantained from pH 1-7, with the addition of 0.1M nitric acid and 0.1M sodium hydroxide where required.Then 25 mg bio-material was taken in seven separate 50 ml sample bottles with 20 ml working solution of Cd (II) and Zn (II) metal ions each with different pH and shaken at room temperature at 150 rpm for 24 h to attain equilibrium. After 24 h, the solutions were filtered and their equilibrium concentrations were measured using ICP-AES (SPECTRO Analytical Instruments, Kleve, Germany).

Effect of Metal ions concentration

The adsorption of Cd (II) and Zn (II) metal ions were carried out taking metal ions of different concentration from 25mg/L to 800 mg/L at their optimum pH. The sample bottles were shaken at room temperature at 150 rpm for 24 h, then the solutions were filtered and equilibrium concentrations were measured using ICP-AES. The quantity of adsorbed metal ions was calculated from the decrease in metal ion concentration using the equation 1. The results obtained were analysed using Langmuir Isotherm[17].

$$q_e = (C_i - C_e) \times \frac{V}{M} \qquad (1)$$

where, q_e (mg/g) is the amount of metal ions adsorbed by the biomaterial, C_i (mg/L) is the initial concentration of metal ions in aqueous solution, C_e (mg/L) is the concentration of metal ions in aquous solution at equilibrium, V (ml) is the initial volume of metal ions and M (g) is the weight of the biomaterial.

Effect of contact time

The effect of contact time on the adsorption of Cd (II) and Zn (II) metal ions were studied from 5 minutes to 6 h. The experiment was carried out taking 25 mg biomaterial along with 20 ml of respective metal ions solutions of 50 mg/L at their optimum pH in 14 different sample bottles. All the bottles were shaken in a shaker for the desired time interval and at the end of each contact time, the solution was filtered, then their concentrations were measured using ICP-AES. The amount of metal adsorbed at time (t) was calculated from the mass balance between initial concentration and concentration at time (t) to analyse the adsorption rates of metal ions onto the biomaterial.

Results and Discussion

The surface morphology of Kush powder was analysed using scanning electron microscope before and after functionalization. The SEM image of raw and charred Kush powder show smooth and even surface as shown in figure (1a) and (1b). Formation of micropores on the surface of AKP was observed as shown in figure (1c) .These changes of structure confirm the chemical modification on the surface of Aminated Kush [18].

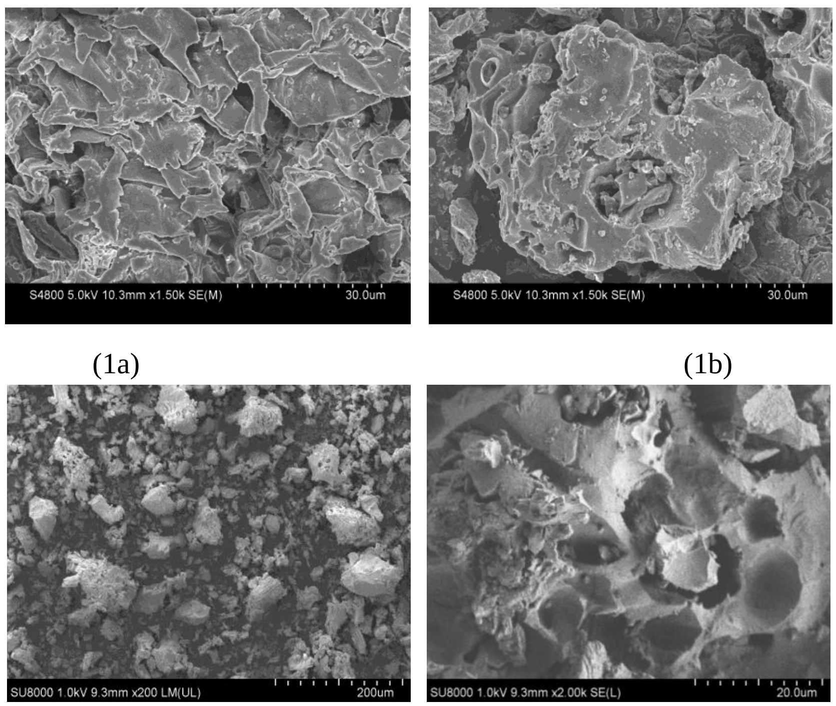
The functional groups present in the Kush powder were analysed with the help of diffuse reflectance infrared spectroscopy (DRIFT) (Harrick Scientific Corporation). The intense sharp adsorption peak at 3409 cm^{-1} in figure 4 indicates the O-H stretching vibration due to inter and intramolecular hydrogen bonding of alcohols, phenols and carboxylic acids, indicating the presence of free hydroxyl groups on the biomaterial surface. Peaks at 2926 cm^{-1} corresponds to C-H stretching vibration, 1736 cm^{-1} stretching vibration of bond due to non ionic carboxylic groups like –COOH and $–COOCH_3$,the peak at 1639 cm^{-1} is due to N-H bending vibration of amines, peak at1124 cm^{-1} is assigned to alcoholic C-O stretching vibration. Peak at 931 cm^{-1} is for glycoside bonds in the polysaccharide structure [22, 23].

After the functionalization of biomaterial, the spectrum exhibits some changes in figure 2. The intense sharp peak at 3409 cm^{-1}in the RKP shifted to 3393 cm^{-1} as a broad peak in AKP, that indicates the overlapping of hydroxyl groups with amine group in AKP. Thus, the broadband peaks confirmed the introduction of amine group onto the surface of funtionalised biomaterial. Some peaks of RKP at 2926 cm^{-1}, 1639 cm^{-1}, 1124 cm^{-1}, 931 cm^{-1} are significantly reduced in AKP.

Elemental analysis shows the percentage composition of elements present in the Kush powder.Carbon and Nitrogen were found to be 41.27 % and 1.13 % in RKP where as 51.47 %

and 5.49 % in AKP respectively. Increase in percentage of nitrogen after functionalization suggests the introduction of amine group in the Kush powder.

pH is one of the major factor which determines the removal capacity of different metal ions from aqueous solution by adsorption.Variation in pH could change the characteristics and availablity of metal ions in solution as well as the surface charge of biomaterial and degree of ionisation. At low pH, adsorption of Cd (II) and Zn (II) metal ions decreased which may be due to the increase in competition between metal ions and H^+ ions for the active sites on the bio-material surface, where as adsorption increased with the increase in pH value of the solution, which may be due to lesser number of surface lagands with negative charges. Maximum adsorption of Cd (II) and Zn (II) were observed at pH 6 as shown in figure 3.



(1a) (1b)

(1c) (1d)

Figure 1: Scanning electron microscope (SEM) photographs of (1a) RKP (1b) CKP and (1c, 1d) AKP.

Study of adsorption Isotherm helps to find the maximum adsorption capacity of the biomaterial. The maximum adsorption capacity of the functionalized biomaterial for Cd (II) and Zn (II) were investigated at the various concentrations from 25 mg/L to 800 mg/L of the respective metal ions.Figure 4 represents a plot of the adsorption amount (q_e mg/g) versus the equilibrium metal ions concentration in the solution (C_e mg/L). Equilibrium data were fitted as shown in figure 5 with the Langmuir adsorption Isotherm which is given by equation 2 [17].

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (2)$$

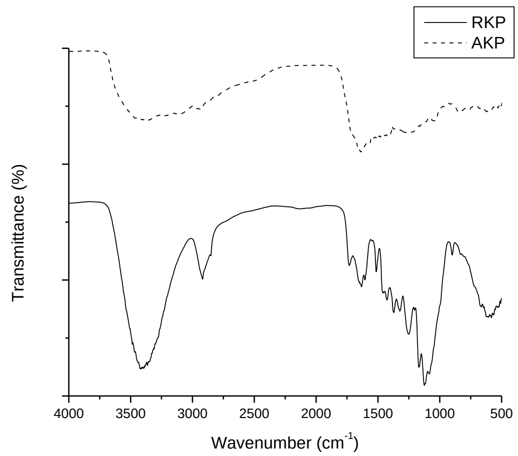


Figure 2: FTIR of (a) RKP and (b) AKP (after functionalization)

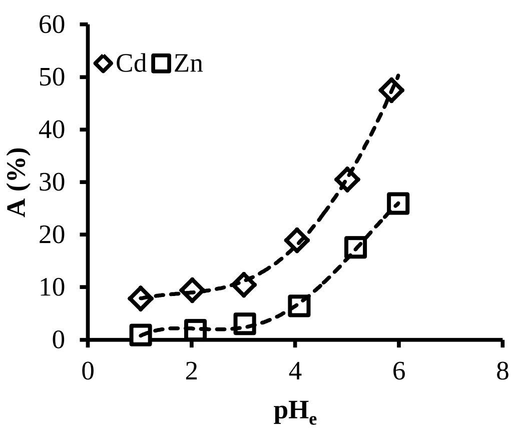


Figure 3: *Effect of pH in the adsorption of Cd (II and Zn (II) onto Aminated Kush powder.*

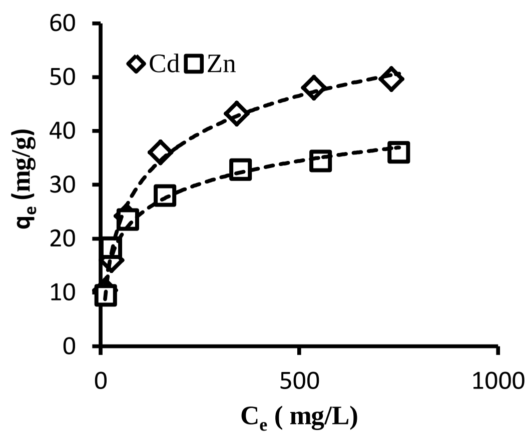


Figure 4: *Adsorption isotherm for Cd (II) and Zn (II) onto Aminated Kush powder.*

where, q_m is the maximum amount of adsorption (mg/g), b is the adsorption equilibrium constant (L/g) and C_e is the concentration (mg/L) of metal ions in solution at equlibrium.

The adsorption increase with increase in equilibrium concentration at low metal ions concentration and tend to approach constant value for each metal ions at their higher concentration, suggesting that these metal ions are adsorbed onto the biomaterial according to Langmuir adsorption. The adsorption of metal ions is eventually limited by the fixed numbers of active sites and a resulting plateau can be observed, which is well described by Langmuir parameter $q_{max.}$ The maximum adsorption capacities evaluated in terms of mg/g of biomaterial are 49.6 mg/g for Cd (II) and 36 mg/g for Zn (II) respectively, which is in close agreement with q_{max} value obtained from the Langmuir plots given in Table 1. The experimental data are in good linear relationships, suggesting that the adsorption sites have equal affinities for the adsorbate molecules.

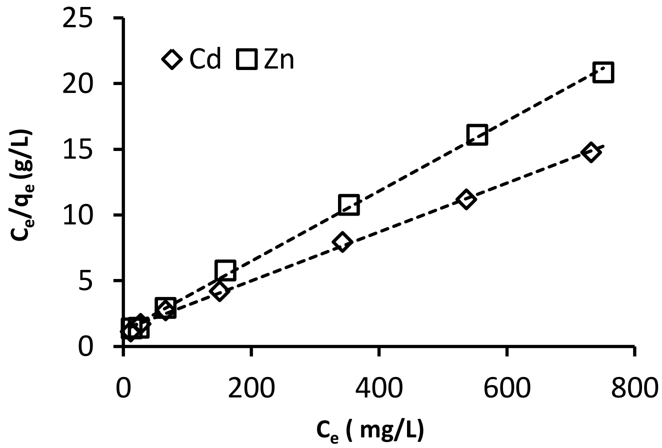


Figure 5: *Langmuir plot for adsorption of Cd (II) and Zn (II) onto Aminated Kush powder.*

Table 1: *Langmuir adsorption isotherm model parameters and experimental q_{max}*

Metal ions	*Langmuir q_{max} (mg/g)*	*Experimental q_{max} (mg/g)*	*b (L/g)*	*R^2*
Cd	*55.56*	*49.60*	*0.014*	*0.998*
Zn	*38.42*	*36.00*	*0.023*	*0.998*

Batch adsorption experiments were carried out for different contact times with a fixed biomaterial dose of 25 mg at their optimum pH 6. The equilibrium is reached between 150-180 minutes of adsorption for respective metal ions and reached a saturation level. As the contact time increased, the active sites on the adsorbents were filled and the adsorption rate became slower and reached the plateau as shown in figure 6.

Table 2: *Sorption kinetics of pseudo second order for Metal ions onto AKP*

Metal ions	R^2	K_2 (g/mg/min)
Cd	0.998	0.0077
Zn	0.998	0.0009

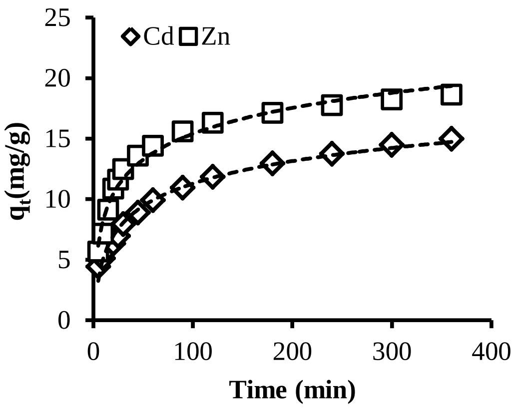


Figure 6: *Adsorption kinetics of Cd (II) and Zn (II) onto Aminated Kush powder.*

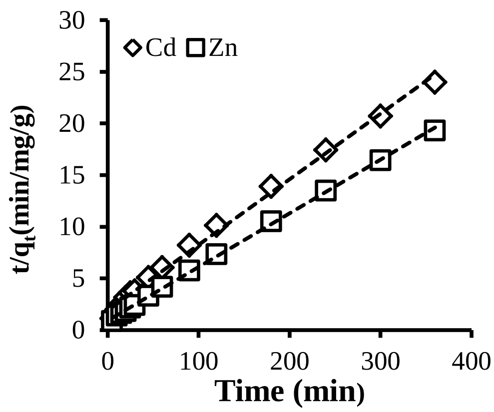


Figure 7: *Pseudo second order kinetic model in the adsorption of Cd (II) and Zn (II) onto Aminated Kush powder.*

Kinetic modeling of the data was studied using pseudo- second order rate equation, and its applicability was tested by linear plot of t/q_t versus t, as shown in figure 7.

The values of rate constant (K_2) for Cd (II) and Zn (II) are 0.0021 and 0.0028, and correlation coefficient are 0.99 and 0.99 for the respective metal ions as given in table 2, which showed that the model can be applied for the entire adsorption process and confirm the chemisorption of respective metal ions onto the AKP.

Conclusions

AKP were prepared from RKP by treating with thionyl chloride followed by dimethylamine.Elemental analysis, SEM and FTIR analysis revealed the introduction of amine groups into the biomaterial which had shown good adsorption capacity for Cd (II) and Zn (II).The adsorption capacity increases with increase in pH upto their optimum pH value. The adsorption performances were fitted well with Langmuir model with correlation coefficient R^2 of 0.99 and the rate of adsorption follows the pseudo second order kinetics. This concludes that the biomaterial with high metal binding capacity after functionalization may find potential application in wastewater treatment for the removal of heavy metal ions.

Acknoweledgements

Authors would like to thank Prof. Dr. P.K. Jha, Central Department of Botany, Tribhuvan University, Kathmandu and Dr. Antonio Masi and his team, Department of Biotechnology, Padova University, Italy for providing necessary laboratory facilities for the experimental work in Italy. Dr. Lok Kumar Shrestha, National Institute for Materials Science, Tsukuba, Japan and

Dr. A.P. Yadav, Central Department of Chemistry, Tribhuvan University, Kirtipur are acknowledged for their help with SEM images.

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