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Research Article

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Adsorptive removal of Cd (II) using NTA modified *Dendrocalamus strictus* charcoal powder

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ABSTRACT

In present study, Nitrilotriacetic acid (NTA) modified Dendrocalamus strictus charcoal powder was investigated as adsorbent for the removal of Cd (II) metal ions from aqueous solutions. The study revealed that the adsorbent dose 2 g/L of NTA modified Dendrocalamus strictus charcoal powder under optimized conditions viz., pH (6), contact time (2h), temperature (25°C) and concentration (50mg/l) of cadmium metal ions exhibited maximum (89.66%) removal of Cd (II) metal ions. Further, genotoxicity studies using Allium cepa root chromosomal aberration assay showed significant reduction in chromosomal aberrations after the adsorption by NTA modified Dendrocalamus strictus charcoal powder. The study proved that NTA modified Dendrocalamus strictus charcoal powder is an excellent adsorbent with high adsorption capacity for the removal of Cd (II) from industrial waste water.

Keywords: Adsorbent, Nitrilotriacetic acid, *Dendrocalamus strictus*, charcoal, genotoxic.

INTRODUCTION

The contamination of wastewater by different toxic heavy metals through the discharge of industrial waste water is an ongoing problem. Some of these heavy metals are toxic even at low concentrations. Presence of heavy metal ions in aquatic bodies is of special concern as these have potential to accumulate in different environment components. It is well known that heavy metals can damage nerves, liver as well as bones and can interfere with the normal functioning of various metallo-enzymes [1]. Among different metals, cadmium is one of the most commonly used metals in different industrial processes. Cadmium is introduced into water bodies as results of smelting, metal plating, cadmium-nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, alloy industries, photographic industries and sewage sludge [2, 3].

Cadmium is known to cause acute and chronic disorders such as "itai-itai" disease, renal damage, emphysema, hypertension and testicular atrophy [4, 5]. On the basis of these health problems, Cd (II) has been included in the red list of priority pollutants by Department of Environment, UK [6] and in the black list of EEC Dangerous Substance Directive [7]. US Environment Protection Agency has also classified Cd(II) as group B1 carcinogen [8]. Cadmium has been designated as category I carcinogen by International Agency for Research on Cancer (IARC). Cadmium has been document to be one among ''big three'' toxic metals, along with lead and mercury.

A significant number of tests involving plants, bacteria, non-mammalian and mammalian systems have been developed for biomonitoring the extent of pollution and to evaluate the genotoxic potential of environmental contaminants [9-13]. Among different test systems available for genotoxicity evaluation, the utility of plant bioassays is well accepted. Among several higher plant bioassays, *Allium cepa* assay is well known and commonly used in many laboratories. The results obtained with this system are in good agreement with the results from other established test systems using prokaryotic as well as eukaryotic system. *Allium cepa* root chromosomal aberrations test provides a rapid screen for the genotoxic effects of chemicals and metal ions.

Various purification methods have been adopted worldwide to solve heavy metal pollution in the environment. These methods include chemical precipitation, membrane processes, solvent extraction, adsorption and biosorption processes. However, these methods do not seem to be economically feasible because of their relatively high costs and developing countries are not able to afford such technologies. Therefore, there is a need to look into alternatives to investigate a low-cost method, which is effective and economical. To overcome this difficulty, there is a strong need to develop economical adsorbents which can be used to solve this problem. Among different methods, adsorption processes are suggested to be selective, effective and cheap and are able to remove very low levels of heavy metals from solutions [14]. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of certain types of contaminants [15-16]. At present years, different types of materials such as fruit wastes [17-18], fly ash [19], clays [20], bark [21], sawdust [21, 22], biomass [23], husks [24], alumina [25] red mud [26] and agricultural wastes [27] are being used as low-cost alternatives to expensive adsorbents. *Dendrocalamus strictus* charcoal is a cheap, widely available and abundant natural material. Considering this, the present study was planned with aim to remove the cadmium metal ions from aqueous solution using unmodified *Dendrocalamus strictus* charcoal powder (UDC) and modified *Dendrocalamus strictus* charcoal powder (MDC) with Nitrilotriacetic Acid (NTA). Several important factors such as pH, initial metal ions concentration, adsorbent dose, contact time and temperature were investigated in the present study. As the adsorbent some time poses their own toxicity, the genotoxic effects of cadmium metal ions before and after the adsorption process was evaluated using *Allium cepa* root chromosomal aberration assay.

EXPERIMENTAL SECTION

2.1. Material

The culms of *Dendrocalamus strictus* were used to prepare the charcoal powder, which were collected from the Botanical Garden, Guru Nanak Dev University, Amritsar, Punjab (India). All chemicals used were of Analytical reagent grade.

2.2. Preparation of adsorbents

For the preparation of the charcoal, pre-weighed *Dendrocalamus strictus* culms were cut into small pieces, washed and dried at room temperature. The culms pieces were then carbonized in Muffle furnace at 450˚C for 2 h to prepare the charcoal and were allowed to cool at room temperature. The charcoal was crushed to form fine powder using grinder and was passed through the sieve of 150 µm. the charcoal powder was divided into two parts. One part of charcoal powder was stored in desiccators for further adsorption experiments and the second part was treated with Nitrilotriacetic acid. 10 g of adsorbent was added to 500 ml of 1% NTA solution and extracted for 24 h at 25 ± 2°C and 100 rpm shaking. After 24 h extraction, solution with *Dendrocalamus strictus* charcoal powder was filtered through *Whatman* filter paper No 1 and rinsed 3 times with double distilled water. After treatment, modified *Dendrocalamus strictus* charcoal sample was oven dried at 60 ± 2°C for 24 h, conditioned at 23 ± 5°C for two weeks and was stored in desiccators for further experiment studies.

2.3. Preparation of the Stock Solution

Stock solution of 1000 mg/l of cadmium was prepared by dissolving 2.744 g of cadmium nitrate ($Cd(NO_3)_2.4H_2O$) in 1000 ml of double distilled water. Different concentrations of cadmium (50, 100, 200, 300, 400 and 500 mg/l) were prepared from the stock solution by making fresh dilution for each adsorption experiment.

2.4. Batch adsorption studies

Adsorption experiments were performed using different concentrations *viz.,* 50, 100, 200, 300, 400 and 500 mg/l of cadmium, pH (1, 2, 3, 4, 5, 6 and 7) temperature (25˚C), contact time (0.5, 1, 2 and 4 h) and dosage (0.1, 0.2, 0.3 and 0.4 g/100 ml) of adsorbents (unmodified *Dendrocalamus strictus* charcoal powder and modified *Dendrocalamus strictus* charcoal powder) at 120 rpm/min in incubator shaker. Different batch experiments were carried out to achieve the optimum conditions for maximum adsorption. The final concentration of the cadmium was analyzed after every batch experiments using Atomic Absorption Spectrophotometer (Model: AA240 FS, Make: Agilent).

Contents of the flask were filtered through *Whatman* filter paper No. 1 and filtrate was analyzed for metal ions concentration. All the experiments were conducted in triplicates.

2.5. Calculation of percentage removal and adsorption capacity

The percent adsorption of the cadmium metal ions was calculated as follows

Percent adsorption (%) = $\frac{c_i - c_f}{c_i} \times 100$

Where 'c_i' stands for initial and 'c_f' stands for final concentrations (mg/l) of cadmium.

2.6. Genotoxicity of cadmium metal ions

Genotoxicity of cadmium was estimated by using *Allium cepa* root chromosomal aberration assay. The bulbs of *Allium cepa* with freshly emerged roots of about 0.5 - 1.0 cm length were treated by placing them on treatment jars containing different concentrations of cadmium metal ions solution corresponding to 50, 100, 200, 300, 400 and 500 mg/l of cadmium for 3 h before and after the adsorption onto the both samples (unmodified *Dendrocalamus strictus* charcoal powder and modified *Dendrocalamus strictus* charcoal powder with NTA). After 3 h, the roots were thoroughly washed and root tips were fixed in Farmer's fluid (glacial acetic acid : ethanol :: 1 : 3). The fixed root tips were hydrolyzed in 1 N HCl with intermittent heating (up to 60˚C) for 1 min and transferred to watch glass containing a mixture 1 N HCl and aceto-orecin (1 : 9) for 25-30 min. Then the root tips were squashed in a drop of 45% glacial acetic acid. The slides were observed for different types of chromosomal aberrations. About 450 dividing cells in 9 root tips (~50 cells/slide) were scored to determine the genotoxic effects of cadmium metal ions in the absence and presence of both samples (unmodifed *Dendrocalamus strictus* charcoal powder and modified *Dendrocalamus strictus* charcoal powder with NTA).

RESULTS AND DISCUSSION

3.1. Effect of pH

pH is consider as an important controlling parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional group of the adsorbent and the degree of ionization of the adsorbate during reaction [28-30]. The effect of pH on cadmium metal ions adsorption onto *Dendrocalamus strictus* charcoal powder (unmodified and modified) was studied at 25 °C by varying the pH of cadmium solution from 1 to 7 (Fig. 1a).

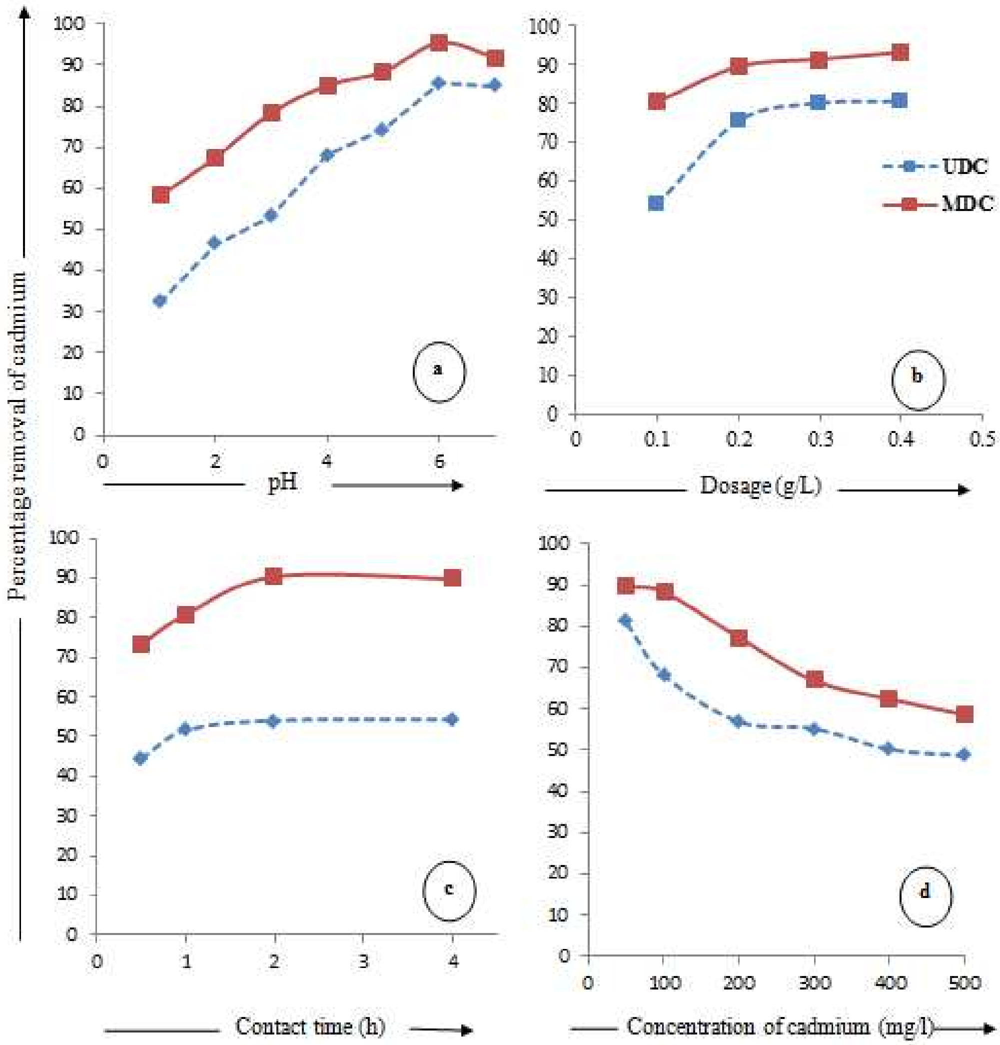

Fig. 1. Effect of pH (a), adsorbent dosage (b), contact time (c) and concentration (d) on the cadmium metal ions removal by unmodified and NTA modified *Dendrocalamus strictus* charcoal powder

It was observed that removal of cadmium by both unmodified and modified *Dendrocalamus strictus* charcoal powder adsorption increased with increasing pH from pH 1 to pH 6 and decreased slightly at pH 7. The maximum adsorption was found to be at pH 6. Therefore for further batch experiments, pH was fixed at 6.

3.2. Effect of adsorbent dose

Adsorbent dose is considered as another important factor affecting the percentage removal of a metal ion. The adsorption of cadmium metal ions onto the both adsorbents (UDC and MDC) was studied at 25 °C temperature and fixed pH value by varying adsorbent dosage from 0.1 to 0.4 g/100 ml. In the present study, the percentage removal of the cadmium metal ions increased with increasing the both adsorbent dosage from 0.1 to 0.2 g/100 ml and after then, remained nearly constant with higher adsorbent dose i.e. 0.3 g/100 ml and 0.4 g/100 ml. Among the both four adsorbent dosages (UDC and MDC) *viz.*, 0.1, 0.2, 0.3 and 0.4 g/100 ml, maximum adsorption of the cadmium metal ions was attained at 0.2 g/100 ml (Fig. 1b). Therefore, the optimum dosage was taken as 0.2 g/ 100 ml for further experiments. Similar results have been found by Wang et al [31] and Gupta and Bhattacharyya [20] for cadmium (II) adsorption onto different clays.

3.3. Effect of contact time
Contact time of adsorbent is one of the important parameters for successful rapid adsorption. Fig. 1c represents the percent removal of cadmium metal ions initially increased rapidly, and that the optimal removal efficiencies *i.e.* 44.43% and 73.43% were attained within 2 h for UDC and MDC, respectively. However, the equilibrium (maximum) value was attained at around 4 h for both UDC and MDC. Therefore, the optimum contact time was selected as 2 h for further experiments. Similar result was observed for the adsorption of cadmium (II) onto clarified sludge [32], food waste [33], meranti wood [34].

Table 1. Removal of cadmium metal ions (%) after the adsorption onto unmodified and modified *Dendrocalamus strictus* charcoal powder

Concentrations (mg/l)	%age removal of cadmium metal ions after adsorption by *Dendrocalamus strictus* charcoal powder	
	Unmodified	Modified
50	81.16±0.001	89.66±0.003
100	68.16±0.001	88.37±0.002
200	56.91±0.003	77.40±0.033
300	55.27±0.003	66.86±0.001
400	50.19±0.003	62.42±0.003
500	48.65±0.003	58.69±0.003

3.4. Effect of initial concentration of cadmium metal ions
The effect of initial concentration on the adsorption of cadmium metal ions (UDC and MDC) was investigated by varying the cadmium concentration (50, 100, 200, 300, 400 and 500 mg/l) as shown in Fig. 1 d. It was observed that adsorption of cadmium metal ions onto *Dendrocalamus strictus* charcoal powder decreased with increasing concentration of the solution (Table 1). At initial concentration, surface area and availability of adsorption sites were relatively high and cadmium metal ions were easily adsorbed. At higher concentration, the total available adsorption sites were limited and resulted in decrease in percentage removal of cadmium metal ions. The removal of cadmium metal ions from aqueous solution was observed to be concentration dependent. This might be due to the increase in driving force of the cadmium metal ions concentration gradient [35]. A similar result has been found in adsorption of cadmium (II) from aqueous solutions on sulfurized activated carbon prepared from nut shells [36] and meranti wood [34].

3.5. Genotoxic studies
Chromosomal aberrations observed in root tip cells of *Allium cepa* under 3 h treatment of different concentration of cadmium metal ions (50, 100, 200, 300, 400 and 500 mg/l), before and after the adsorption onto the *Dendrocalamus strictus* charcoal powder (UDC and MDC) were categorized into two groups as physiological aberrations (attributing to changes in cell milieu or normal functioning of spindle apparatus) and clastogenic aberrations (attributing to direct action on chromosomes) (Fig. 2).

The physiological aberrations included c-mitosis, also known as spindle inhibition resulting in random scattering of chromosomes over the cell; delayed anaphases in which two anaphasic groups of chromosomes lie close to each other near equatorial plate; stickiness which may be attributed to changes in the surface nucleoprotein configuration; vagrant chromosomes, a weaker c-mitotic effect when one or two spindle fibers are not functioning properly or are not formed. The clastogenic aberrations included chromosomal breaks and chromatin bridges which may be formed due to unequal exchanges resulting in the formation of dicentric chromosomes which are pulled equally to the both poles.

The frequency of chromosomal aberrations following treatment with different concentrations of cadmium before the adsorption by *Dendrocalamus strictus* charcoal powder ranged from 21.74% at 50 ppm to 43.30% at 500 ppm. The frequency of cells with c-mitosis was found to be maximum followed by delayed anaphases, stickiness, vagrant chromosomes, chromosomal break/s and chromatin bridges. The frequency of root tip cells with physiological aberrations was found to be more as compared to clastogenic aberrations. In earlier studies, sensitivity to Cd toxicity has been reported among different plant species [37, 38].

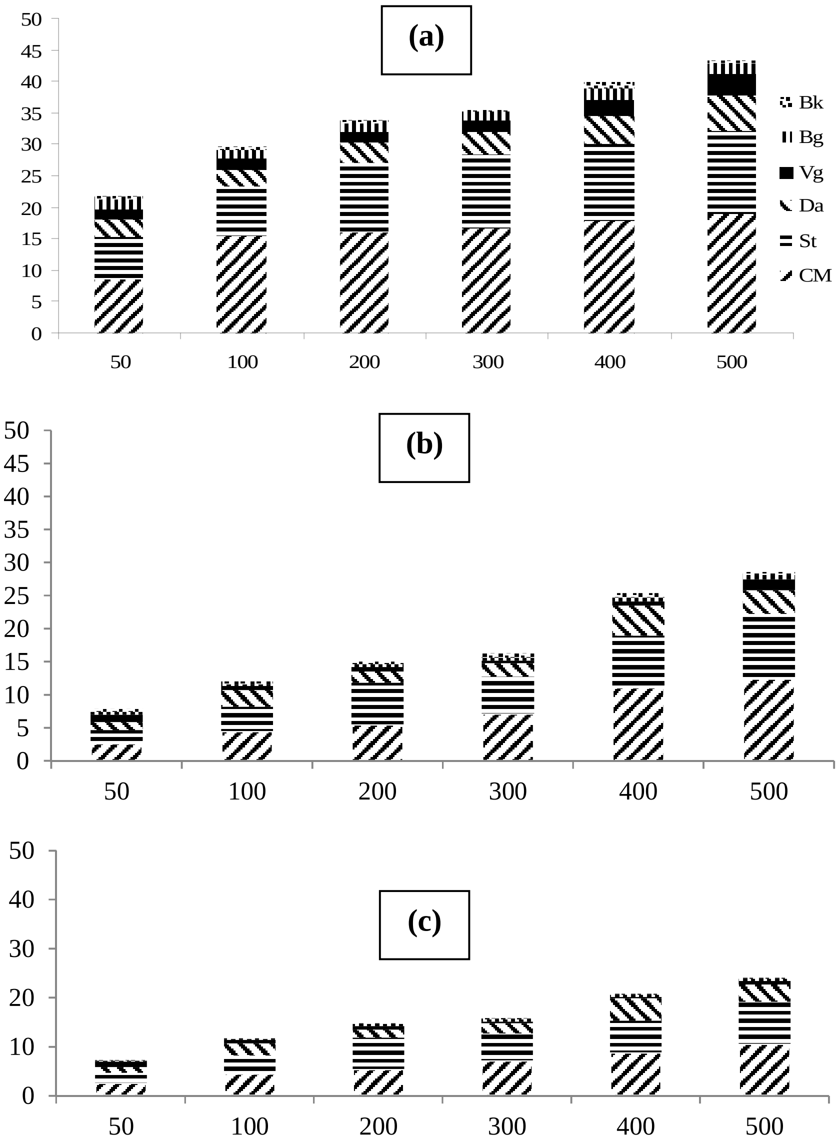

Fig. 2. Spectrum of chromosomal aberrations induced in root tip cells of *Allium cepa*.
(a) Before adsorption of cadmium metal ions
(b) After adsorption of cadmium by unmodified *Dendrocalamus strictus* charcoal powder
(c) After adsorption of cadmium by modified *Dendrocalamus strictus* charcoal powder with Nitrilotriacetic acid

Bk- Chromosomal break/s; Bg- Chromatin bridge/s; Vg Vagrant chromosome/s; St-Stickiness; Da-Delayed anaphase/s; Cm-C-mitosis

Reduction in the chromosomal aberrations was observed after the adsorption of cadmium metal ions by *Dendrocalamus strictus* charcoal powder (UDC and MDC). The total aberration frequency including both physiological as well as clastogenic aberrations after the adsorption by unmodified *Dendrocalamus strictus* charcoal powder ranged from 7.89% at 50 ppm to 28.61% at 500 ppm and adsorption by modified *Dendrocalamus strictus* charcoal powder ranged from 7.32% at 50 ppm to 24.07% at 500 ppm. Maximum reduction in chromosomal aberrations was observed after the adsorption by modified *Dendrocalamus strictus* charcoal powder than unmodified *Dendrocalamus strictus* charcoal powder (Table 2).

Table 2. Genotoxic potential of cadmium metal ions in *Allium cepa* root chromosomal aberration assay before and after the adsorption by *Dendrocalamus strictus* charcoal powder

Concentrations (mg/l)	%age chromosomal aberrations		
	Before adsorption	After adsorption	
		Unmodified	Modified
50	21.74±0.003	7.89±0.003	7.32±0.006
100	29.52±0.005	12.05±0.003	11.72±0.006
200	33.76±0.005	15.07±0.006	14.86±0.003
300	35.52±0.003	16.31±0.006	15.87±0.006
400	39.74±0.003	25.37±0.006	20.83±0.006
500	43.30±0.003	28.61±0.006	24.07±0.003

CONCLUSION

Batch experiments for the adsorption of cadmium metal ions from aqueous solutions have been carried out using *Dendrocalamus strictus* charcoal powder (unmodified and modified) as adsorbent in the present study. The study revealed that at pH 6, 2 g/L of adsorbent material, contact time 2h, temperature 25°C and concentration (50mg/l) of cadmium metal ions, the percentage removal of Cd (II) was maximum (89.66 %) for NTA modified *Dendrocalamus strictus* charcoal powder. Total aberration frequency after the adsorption by unmodified *Dendrocalamus strictus* charcoal powder ranged from 7.89 % at 50 ppm to 28.61 % at 500 ppm while after adsorption by modified *Dendrocalamus strictus* charcoal powder, it ranged from 7.32 % at 50 ppm to 24.07 % at 500 ppm. The results revealed that NTA modified *Dendrocalamus strictus* charcoal powder could be employed as a promising and effective adsorbent for the removal of cadmium from aqueous solution.

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