ORIGINAL ARTICLE

REMOVAL OF CADMIUM FROM INDUSTRIAL WASTE WATER BY USING BIOMATERIALS.

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ABSTRACT

BACKGROUND: ***The heavy metal pollution and toxic organic compounds are of greater concern for human and environmental health because of discharges to water, air, and the terrestrial environment. Cadmium is one of the heavy metal, which is non-essential for microorganisms and other life forms and exerts toxic action on them after cellular uptake. There are reports concerning morphological, biochemical, toxicological and physiological changęs caused by cadmium in microorganisms. Cadmium may influence heart diseases in human beings. Therefore, proper treatment of industrial wastewater is essential before releasing into the recipient environment. The aim of the present research work is to find a newer eco-friendly wastewater treatment technology mainly concerning the removal toxic elements in the contaminated water system.***

METHODS: ***A synthetic wastewater sample was prepared and real samples were collected. Activated carbon of Tridax procumbens (Asteraceae; Compositae), was used as biomaterial. Batch adsorption experiments were performed for determination of contact time, effect of adsorbent dose, control of pH and temperature. Cadmium ion – specific electrode system was used for the analysis of free cadmium ion concentrations in test samples.***

RESULTS: ***In the present investigation, the rate of removal of Cd (II) ions in synthetic wastewater is mainly controlled by pH of the solution. The adsorption starts at pH 3.5 and steeply rises to 6.5. At this pH 98 percent, removal of Cd (II) was achieved. The optimum contact time was estimated to be 180 minutes and the amount of bioadsorbent used was 4.0g. The removal of Cd (II) was completed within 90 minutes in dilute solutions of 25 PPM. However, at higher concentrations (50 and 100 PPM), the removal was completed only after 120 and 180 minutes, respectively. In real sample analysis, complete removal of Cd (II) was achieved by using 4.0g of activated carbon of the bioadsorbent within 180 minutes of contact time.***

CONCLUSION: ***The biomaterial employed in this experimental study is harmless to human beings. The percent removal of Cd (II) under the conditions employed here, is 98 with an effective dose of 4.0 g of bioadsorbent. Complete removal of Cd (II) in electroplating unit wastewater is achieved. This process can be effectively used in Cd (II) and other heavy metals removal in industrial wastewater.***

KEY WORDS: ***Industrial wastewater, cadmium removal, bioadsorbent, eco-friendly technology.***

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INTRODUCTION

Trace metals occur naturally in rocks and soils and these metals accumulate locally in soils due to in situ weathering of rock mineral. There are generally higher quantities of metals in igneous than in sedimentary rocks. Igneous and metamorphic rocks are the commonest natural source of trace metals in soil. Apart from metals originating in parent geological materials and entering the soil through chemical weathering processes, there are many anthropogenic sources of toxic metals. Increasingly higher quantities of certain trace metal are being released into the environment by anthropogenic activities primarily associated with industrial processes, manufacturing and the disposal of industrial and domestic refuse and waste materials (1-3).

Although all trace metals are released in varying quantities into soil from parent materials, significant amounts of certain soil metals are derived from other sources, particularly atmospheric deposition (mainly Pb and Zn) and agricultural amendments mainly Cd (4). Smaller amounts of other metals arrive in soil from atmospheric deposition, although there are many reports of local concentrations due to fallout near point sources such as metal smelters (5, 6) and or mining activities (7).

Sewage sludge contains larger concentrations of heavy metals than most soils, and once the metals have entered the soil they are not easily leached. Therefore, disposal of sludge to land results in an accumulation of these potentially toxic elements in topsoil. Because of this, and in the light of new information on adverse effects of sludge-derived metals on soil microbial processes, it may be necessary to re-appraise the limits for metal concentrations in sludge-treated soils (8).

Studies of the effects of metals on the yield and quality of plant produce from sludge treated soils began earlier and a general consensus has emerged about the measures needed to protect against phytotoxicity and adverse effects on the food chain (9); possible exception are Cd and Cr. Sewage sludges usually contain much more Zn, Cu, Ni, Cd, Cr and Pb than soils, so the emphasis will be on these metals. However, Cr and Pb are so insoluble in sludge-treated soils that they are unlikely to be bioavailability and cause adverse effects (10).

Cadmium is one of the heavy metal, which is non-essential for microorganisms and other life forms and exerts toxic action on them after cellular uptake. In small amounts, trace elements are normal constituents of fresh water organisms but at higher concentrations, they exert ranges of toxic effects. There are reports concerning morphological, biochemical, toxicological and physiological changes caused by cadmium in microorganisms (11 - 16). Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years although it is eventually excreted. Cadmium strongly adsorbs to organic matter in soils. When cadmium present in soils it can be extremely dangerous, as the uptake through food will increase. Cadmium is known for their toxicity in organisms because it is similar in physical as well as chemical properties with calcium; hence, it replaces calcium in bone and skeleton (17). In humans, long-term exposure is associated with renal disinfections. High exposure can lead to obstructive lung disease and has been linked to lung cancer. The average daily intake for humans is estimated as 0.15μg from air and 1μg from water. Cadmium may influence heart diseases in human beings. According to USEPA and WHO, the maximum contaminant level (MCL) in drinking water is 0.01 mg/L (18).

The toxic actions of trace elements occur due to bioaccumulation and biomagnifications of the elements in tissues of living organisms (19 – 21). The heavy metal pollution and toxic organic compounds are of concern for human and environmental health because of discharges to water, air, and the terrestrial environment (22). Discharges of different effluents may lead to localized soil pollution through the accumulation of potentially toxic elements (23, 24). Hence, proper treatment of industrial wastewater is essential before releasing into the recipient environment.

There are several methods available for the removal of heavy metals from the industrial wastewater (25 - 28). However, most of the conventional methods generate secondary effluent impacts on the recipient environment; mainly microbial bioadsorbent methods are economically not feasible. The extensive literature survey reveals that, no sufficient information is available for the removal of cadmium ions from water and wastewater. In this context, the application of plant leaves, (Phytoremediation technology) is an emerging methodology, considered for the removal of cadmium in contaminated systems because of its cost effectiveness and long-term applicability. In our earlier research studies, we have used novel biomaterials; Tridax procumbens (Asteraceae) a medicinal plant largely populated in southern part of Tamilnadu, India for the color removal of industrial wastewater (29). The aim of the present research work is to test the applicability of the plant biomaterial for the removal of cadmium in the industrial wastewater.

MATERIALS AND METHODS

Preparation of synthetic wastewater

Synthetic wastewater samples were prepared by using analytical grade Cd $(NO_3).4H_2O$ by using double distilled water. The concentration of the solution was 0.1M. The stock solution was prepared by dilution with double distilled water, which contains 100 ppm of Cd^{2+} ions. The pH of the solution adjusted to 6.5 by using dilute sulphuric acid.

Preparation of activated carbon of the bioadsorbent

Raw bioadsorbent was collected from the agricultural field, air-dried and powdered. The homogeneous powder was used for the experiments. Activated carbon of the biomaterial was prepared by treating with the concentrated sulphuric acid (Sp.gr.1.84) in a weight ratio of 1:1.8 (biomaterial: acid). The resulting black product was kept in an air – free oven maintained at $160^0 \pm 5^0C$ for 6 hours followed by washing with distilled water until free of excess acid dried at $105^0 \pm 5^0C$. The activated carbon obtained from biomaterial was ground and the portion retained between 90 and 125 μm sieves was used for metal adsorption experiments (30). The results of characterization of bioadsorbent were presented in table – 1.

Table 1. Characterization of bioadsorbent.

Parameters	Results
Bulk density (g/mL)	0.75
Moisture (%)	0.50
Ash (%)	0.70
Solubility in water (%)	0.45
Solubility in acid (%)	1.0
pH	7.55
Decolorizing power (mg/g)	0.55
Phenol number	35.65
Surface area (m^2/g)	320
Iron (%)	0.75

Batch Adsorption Experiments

The batch experiments were performed by adding 100 mL of synthetic Cadmium solutions of different predetermined concentrations in ten 250 mL stoppered conical flasks. One of the experimental flask may used as control experiment. A definite quantity of the bioadsorbent was added to the reaction flasks and shaken in a mechanical shaker for definite period. Adsorbent dose and shaking time were optimized by continuous variation method. After equilibrating, the system was allowed to settle for 30 minutes, filtered and analyzed for cadmium. The difference in the cadmium content before and after adsorption experiments represents the amount of cadmium adsorbed by the bioadsorbent. All the experiments were performed at room temperature (30°C). Higher temperature and uncontrolled agitation may affect the cadmium ion removal process. The duration of the experiments was 220 minutes. The free ion concentrations of Cd^{2+} in the test solutions were measured by Orion cadmium – specific electrode (Model 94 – 98) connected to a digital ion analyzer. The mechanism involved in the removal of cadmium ion is the chemical adsorption process.

Testing of industrial wastewater

Cadmium electroplating industry wastewater samples were collected and diluted properly. and adsorption experiments were performed for the removal of heavy metals. The results of characterization of industrial wastewater were presented in table – 2.

Table 2. Characterization of Industrial wastewater.

Parameters	Results
pH	3.5
Electrical conductivity (μmhos/cm)	4387.50
Total dissolved solids (mg/L)	6750
Turbidity (NTU)	1.25
COD (mg/L)	35
Chloride (mg/L)	475
Sulphate (mg/L)	1250
Iron (mg/L)	38
Cadmium (mg/L)	950
Calcium (mg/L)	85
Sodium (mg/L)	175
Potassium (mg/L)	30

The experimental condition for the removal of cadmium ion was similar to that of synthetic water samples.

The percent removal of selected heavy metals on the adsorbents calculated from

$$\% \text{ removal} = \frac{C_o - C_f}{C_o} \times 100$$

Where C_o is the initial concentration of metal ions and C_f is the final concentration metal ions in ppm. The main advantage of this method is the recovery of the bioadsorbent after use quantitatively by using desorption techniques. Further, the efficiency of the adsorbent material is excellent.

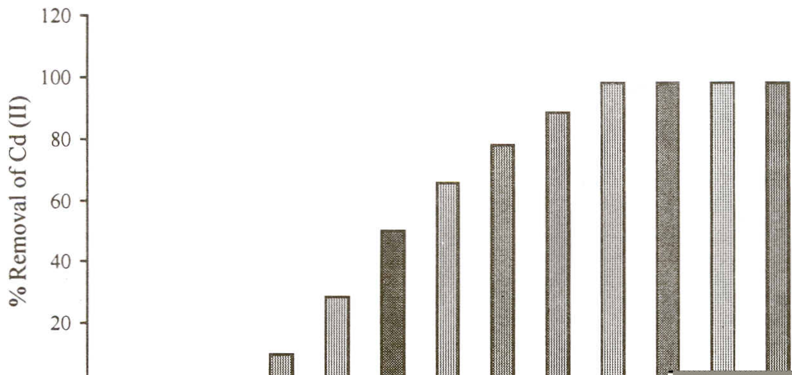
RESULTS

In the present investigation, the rate of removal of Cd (II) ions in synthetic wastewater is mainly controlled by pH of the solution. The adsorption starts at pH 3.5 and steeply rises to 6.5. At this pH 98 percent, removal of Cd (II) was achieved. The optimum contact time was estimated to be 180 minutes and the amount of bioadsorbent used was 4.0g. The analytical results of effect of initial concentrations of Cd (II) ions indicates that metal ion adsorption purely depends on the amount of activated carbon of the bioadsorbent and contact time. The removal of Cd (II) was completed within 90 minutes in dilute solutions of 25 ppm. However, at higher concentrations (50 and 100 ppm), the removal was completed only after 120 and 180 minutes respectively. In real sample analysis, complete removal of Cd (II) was achieved by using 4.0g of activated carbon of the bioadsorbent within 180 minutes of contact time.

DISCUSSION

Effect of pH and temperature on the adsorption

In these studies, the effect of pH on the adsorption of Cd (II) ions on the activated carbon of the bioadsorbent was studied by using the initial concentration of the experimental solution as 100ppm. The adsorbent dose was optimized and fixed as 4.0g. The maximum adsorption of Cd (II) on the surface of the bioadsorbent was 98 percent. The desired pH value for this achievement was 6.5. At this pH level, cadmium ion will not be precipitated in any form. The analytical results are presented in figure 1. It is a well-known fact that upon increasing the temperature, the rate of adsorption also increases (30).



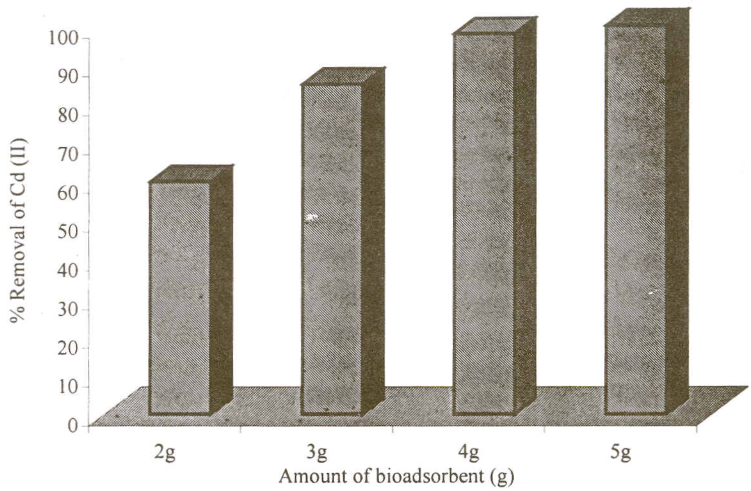


Fig 2. Effect on amount of bioadsorbent on adsorption

Effect of contact time on the adsorption

After optimization of the bioadsorbent dose as 4.0g per 100 ml test solution and the pH at 6.5, the effect of contact time for the efficient removal of Cd (II) ions was studied. When the time of agitation increases, the percent removal also increases. In these studies, 98 percent removal was achieved at 180 minutes. Further, no significant changes were observed in the removal of Cd (II) ions from the solution after 24 hours of equilibration. The analytical results are presented in figure 3.

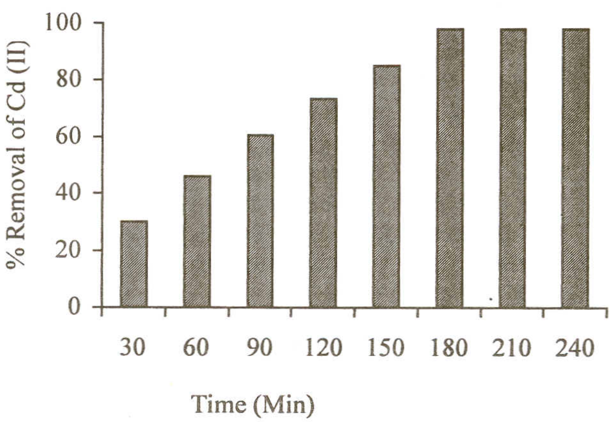


Fig 3. Effect of concentration of Cd (II) ions

Effect of concentration of Cd (II) ions

In the present study, we have selected 10 ppm, 25 ppm and 50ppm as initial concentration for the comparative study for the removal of Cd (II) At 4.0 g of the activated carbon of the bioadsorbent, the effect of the concentration of Cd (II) on the removal of Cd (II) from solution was tested. The removal of Cd (II) was completed within 90 minutes in dilute solutions of 10 and 25 ppm. However, at higher concentrations (50 and 100 ppm), the removal was completed only after 120 and 180 minutes respectively. This observation clearly indicates that the removal of Cd (II) purely depends on the amounts of adsorbents and contact time. The analytical results are shown in figure4.

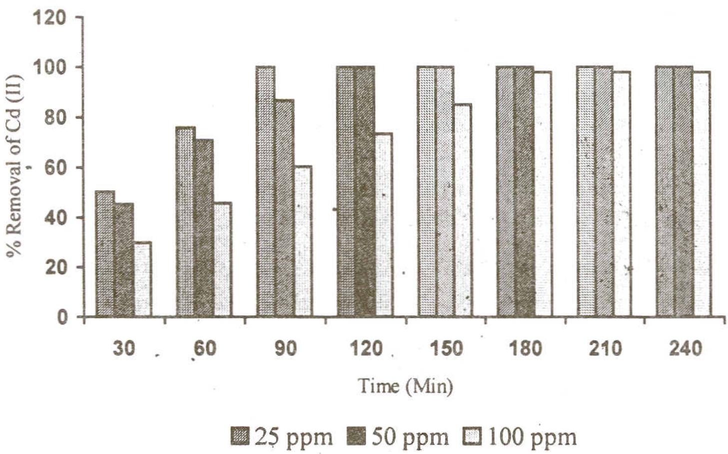


Fig 4. Effect of concentration of Cd (II) on adsorption

Fig 4. Effect of concentration of Cd (II) on adsorption

Removal efficiency of raw bioadsorbent

In the present study, finely powdered raw bioadsorbent was used for testing the efficiency of removal of Cd (II) ions from the experimental solution. The amount of adsorbent dose was 4.0g. The experimental conditions were maintained similar to those of the experiments with activated carbon of the bioadsorbent. The results of the study indicate that around 60 percent removal of Cd (II) was possible. But the chemical oxygen demand (COD) of the resulting solution increases to a large extent. The recorded value of COD was 1250 ppm. Hence, it is not advisable to use the raw bioadsorbent for removal of heavy metals from industrial wastewater.

Treatment of industrial wastewater

The suitability of the bioadsorbent materials for the removal of Cd (II)) was tested with the electroplating industry wastewater. The wastewater sample pH value was maintained as 6.5. The effect of contact time with the adsorbent dose of 4.0 g on Cd (II) removal is shown in Figure 5.

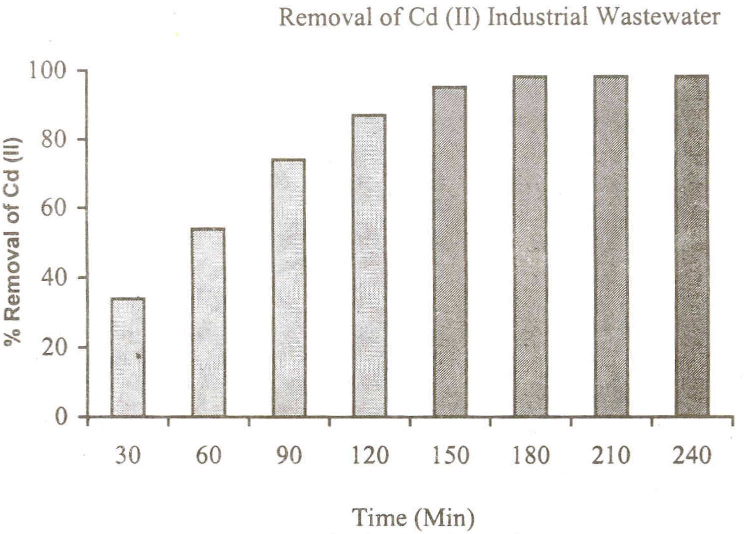


Fig 5. Removal of Cd (II) Industrial wastewater

It has been found that increase in contact time increased the percentage adsorption. The data reveals that the treatment of Cd (II) in industrial wastewater is significantly good. Almost complete removal of Cd (II) from wastewater was possible with 4.0g of the selected bioadsorbent. Thus, the results are in good agreement with the results obtained from the batch experiments conducted for the Cd (II) removal in synthetic wastewater samples.

CONCLUSION

The removal of Cd (II) in synthetic wastewater by using bioremediation technology was studied in batch experimental systems. Based on the results, the following conclusions can be drawn.

- Activated carbon is an efficient biomaterial for removal of cadmium from industrial wastewater.
- The percent removal of Cd (II) under the conditions employed here, is 98 with an effective dose of 4.0 g of bioadsorbent.
- Complete removal of Cd (II) in electroplating unit wastewater is achieved.
- This process can be effectively used in Cd (II) and other heavy metals removal in industrial wastewater.
- The raw bioadsorbent is not suitable for the direct industrial wastewater treatment operation.
- Preliminary treatment of the industrial wastewater is essential before application of activated carbon of the bioadsorbent.
- This methodology can be applied to the removal of toxic metals from the wastewater effectively.

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