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Investigation on the removal of bivalent cadmium ions from aqueous solution and treatment of industrial wastewater using new alumina interfaced biocarbon

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ABSTRACT

The presence of heavy metals in water and wastewater is becoming a severe environmental and public health concern. It may contribute variety of adverse environmental and human health effects due to their acute and chronic exposure through air, water and food chain. They are released into the aquatic environment from many industrial activities. The present research paper deals with the adsorption capacity of the biocarbon material produced from the leaves of *Lawsonia inermis* plant. The biocarbon was prepared by the H_2SO_4 activation process. The adsorption capacity of the biocarbon was evaluated by considering the effect of various parameters such as pH of the solution, biocarbon dose, contact time, and initial metal ions concentration and to optimize the conditions for maximum adsorption. The metal ion uptake capacity of the biocarbon was tested in the stimulated wastewater containing bivalent cadmium ions. The maximum uptake of 97.85% of the Cd (II) metal ions was observed at the equilibrium time of 3.0 hours at a dose of 3.0 g and at the pH of 4.5 in the stimulated wastewater. In the real sample analysis, electroplating industry wastewater is used for the removal of cadmium (II) ions. The results indicate that 95.16% of ions were effectively removed at the same experimental conditions. It is also further noted that the metal sorption capability of the adsorbent is higher with rising concentration of metal ions in the solution. The percentage of adsorption of the metal ions was also significantly increased with rise of temperature of the wastewater.

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INTRODUCTION

The presence of cytotoxic metals in environment is a serious concern. Toxic metal pollutants are discharged into the environment as a consequence of different industrial, aquaculture and other human-made activities [1]. Toxic metals are considered to be non-biodegradable as well as of an extremely poisonous nature [2]. Water pollution and environmental degradation is mainly caused by the release of untreated industrial wastewater containing a lot of toxic substances and some other organic contaminants. Hence, the receiving water bodies are highly contaminated and the quality of the water is changed and become unfit any potable uses [3]. This might cause severe pollution problems. The treatment of industrial wastewater prior to discharge into natural water bodies is therefore very important [4, 5]. Cadmium is one of the toxic metal. It is mainly used in many industrial applications. The long-term exposure of cadmium to human beings may lead to serious renal dysfunction and acute disorders like testicular atrophy, hypertension, bones and kidney damage [6].

In drinking water, the maximum permissible limit (MPL) of cadmium is 0.005 mg/L, as set out in the WHO guideline [7]. The removal of toxic wastewater containing cadmium is therefore essential. In industrial wastewater treatment process numerous technologies are available and some of them are often used to treat contaminated wastewater. However, most of the currently available methods are not efficient in eliminating heavy metals completely at very low concentration. Moreover, the conventional methods are relatively expensive and further produce the secondary effluent and create additional pollution in the aquatic ecosystem. Simple and green techniques are therefore required for the treatment of industrial wastewater. It is well established that adsorption and biosorption techniques are the simplest and most versatile methods used for the water and wastewater treatment. However, the problem of finding low-cost and effective adsorbent materials is still problem in this fields. Many of the adsorbent materials are very costly and reusable.

In these aspects, it is necessary to search for new and low-cost materials for the treatment of the wastewater system. In this field of research, materials such as crab shell [8], coconut copra meal [9], eggshell [10], papaya wood [11], sunflower stem [12], and tea leaves [13] are reported as a cheaper adsorbent for the removal and recovery of toxic heavy metals in wastewater. In the present research work, *Lawsonia inermis* leaves are used for the production of biocarbon and are further used for the elimination of cadmium ions in stimulated wastewater and for their implementation to real wastewaters.

MATERIALS AND METHODS

Preparation of metal solution

The stock solution (1000 mg/L) of cadmium (II) ion was prepared by dissolving the analytical grade of cadmium nitrate Cd $(NO_3).4H_2O$ in double distilled water. The pH values of the working solutions have been adjusted using 0.1 N NaOH and 0.1 N HCl. The pH of the resulting solutions was measured with Hanna pH Instruments (Italy). The concentration of cadmium (II) ions determined by use of AAS.

Preparation of biocarbon

The *Lawsonia inermis* medicinal plant leaves have been collected and air-dried for 48 hours. Biocarbon was produced by the treatment of leaves with concentrated analytical grade sulphuric acid. The resulting black product was kept in hot air oven at 160 $\pm$ 2 °C for 6 hours, then washed with distilled water and then dried at 105 $\pm$ 2 °C. Biocarbon particle sizes between 85 and 130 μm have been used. In a 500 mL beaker, pure alumina and biocarbon were taken at a ratio of 2:1 and double distilled water was added and heated at 60 ^{o}C for 30 min and the resulting product was filtered and dried at 200 $\pm$ 2 ^{o}C for 3 hours. The hot air-dried material is finely ground in a range of 100 to 120 microns and maintained in a separate glass container for further use. The biocarbon material is known as alumina interfaced biocarbon (AIBC).

Batch adsorption process

Batch-wise adsorption experiments were conducted in a series of 250 mL of Erlenmeyer flasks. In the adsorption experiments, the effect of pH, contact time, amount of biocarbon dose and temperature was estimated using an initial metal ion concentration of 100 mg/L with a volume of 100 mL. For the optimization of the amount of adsorbent dose, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g of biocarbon was treated separately with 4.5 pH test solutions. All adsorption experiments were performed at 30 $\pm$ 2°C with the exception of the effect of temperature studies. At 250 rpm, the experimental flasks were constantly agitated up to 180 min to determine the equilibrium condition. Samples were collected at the end of the pre-determined time period (30 min) and the concentration of metal ions was estimated using the AAS technique. Percent removal of cadmium (II) ions and the quantity of metal ions adsorbed from the wastewater system was calculated using the Equations (1) and (2) described by Dada et al., [14]:

$$q_e = \left(\frac{C_o - C_e}{w}\right) \times V \quad (1)$$

$$\%\ Removal = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (2)$$

Where C_o and C_e are the initial and equilibrium concentrations of the metal ions (mg/L), w is mass of biocarbon (g) and V is the volume of the metal containing wastewater (mL) respectively.

Temperature studies

The impact of temperature was explored using 100 mL of sample solution with an initial concentration of 100 mg/L of Cd (II) ions for 3 hours at an optimised adsorbent dose of 3.0 g at temperatures with 30, 40, 50, 60, 70 and 80 °C respectively.

Desorption experiments

The desorption of the Cd (II) ion study was performed using one of the biocarbon used in the batch process. In these experiments, 50 mL of distilled water was added to the spent biocarbon and the pH of the solution was changed to 5.5 with the 1.0 N HCl and the solution was agitated at 250 rpm for 3 hours. The desorbed cadmium ion in the bulk solution was estimated at an interval of 30 min.

RESULTS AND DISCUSSION

Characterization of biocarbon (AIBC)

The characterization of biocarbon is extremely necessary to ascertain the correct surface assimilation capability of the adsorbents in any metal particle removal method. The necessary physico-chemical properties of the *Lawsonia inermis* plant leaves biocarbon are shown in Table 1.

Effect of pH

The pH is a controlling parameter and plays a greater role in the process of biocarbon adsorption of heavy metals. The principal driving force for metal ion adsorption on the adsorbent surface is the electrostatic interaction between adsorbent and adsorbate. The greater the interaction, the higher the adsorption of heavy metal ions. The pH greatly influences the surface charge of the adsorbent and the degree of ionization of heavy metals in solution [15]. The trend of removal of Cd (II) ions to the AIBC surface was shown in Figure 1. The results indicate that the metal uptake is less near pH 3.0. This is due to the repulsive as well as competitive behaviour of H+ ions with Cd (II) ions on the adsorbent surface. This process delayed the Cd (II) ions to reach the binding sites. In addition, Cd (II) ions were precipitated as Cd $(OH)_2$ at the higher pH. The results clearly show that 97.85 per cent of metal ions were removed from the wastewater at the pH of 4.5 per 100 mg/L. The results further reveals that the ion - exchange mechanism was involved during the adsorption of metal ions on the surface of the biocarbon.

Effect of contact time

This is the time needed to achieve equilibrium in the adsorption progression and is also called equilibrium time [16]. The effect of contact time on the removal of Cd (II) ions was investigated by varying the contact time (30-210 min), while other parameters were kept constant. The elimination of Cd (II) ions on the adsorbent matrix is shown in Figure 2. The results show that the elimination of metal ions increased significantly when the contact time increased from 60 to 180 min. The adsorption process is initially rapid due to the accessibility of rich active sites on the adsorbent [17]. The similar findings were also observed by Tong et al., [18]. The mechanism of transfer metal ions to the surface of the adsorbent includes diffusion through the fluid film around the adsorbent particle and through the pores to the internal adsorption sites. In these experimental studies, it is observed that the equilibrium was reached in 180 min. Experimental solutions were left for 24 hours of contact time, but no significant changes were noted in the removal of metal ions.

Effect of amount of biocarbon

The adsorption capacities for different biocarbon doses were determined by keeping all other factors constant, for example, pH, contact time and temperature. The sorption process of Cd (II) ions on the surface of the biocarbon with respect to the initial concentrations of metal ions can be seen in Figure 3. The results show that the uptake of cadmium ions on the surface of the adsorbent was gradually increased from 0.5 g to 4.0 g. This may be due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent. Maximum removal of metal ions was observed at an adsorbent dose of 3.0 g. Further increasing the amount of the adsorbent will not show any significant changes in the removal process. Additionally, the study clearly demonstrates that 3.0 g of the adsorbent is sufficient to remove metal ions. The findings demonstrates that the elimination efficiency of adsorbents is mainly related to the availability of more active sites [19].

Effect of the initial concentration of Cd (II) ions

The initial concentration of Cd (II) provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases. It is mandatory to investigate the role of the initial concentration of metal ions in sorption studies. This is because the contamination of water and wastewater has various metal ion concentrations [20]. Removal of Cd (II) from solution was studied at concentrations of 10, 25, 50, 75 and 100 mg/L, respectively. The percentage of Cd (II) adsorption is shown in Figure 4. The extent of metal ions adsorbed by biocarbon is greatly increased when the initial concentration of metal was enhanced from 10 mg/L to 100 mg/L. In addition, the increasing in uptake capacity of biocarbon with the increasing of Cd (II) ion concentration

Table 1: Physico-chemical properties of biocarbon.

S.No.	Parameters	Values
1.	Moisture content (%)	54.30 ± 1.25
2.	Bulk density (g/ml)	0.98 ± 0.06
3.	Total loss of ignition (%)	96.35 ± 1.16
4.	Total organic components (%)	88.56 ± 1.31
5.	Insoluble components (%)	13.25 ± 1.72
6.	Surface area (BET) (m2/g)	9.65 ± 0.08
7.	C content (%)	86.44 ± 1.08
8.	H content (%)	9.38 ± 0.04

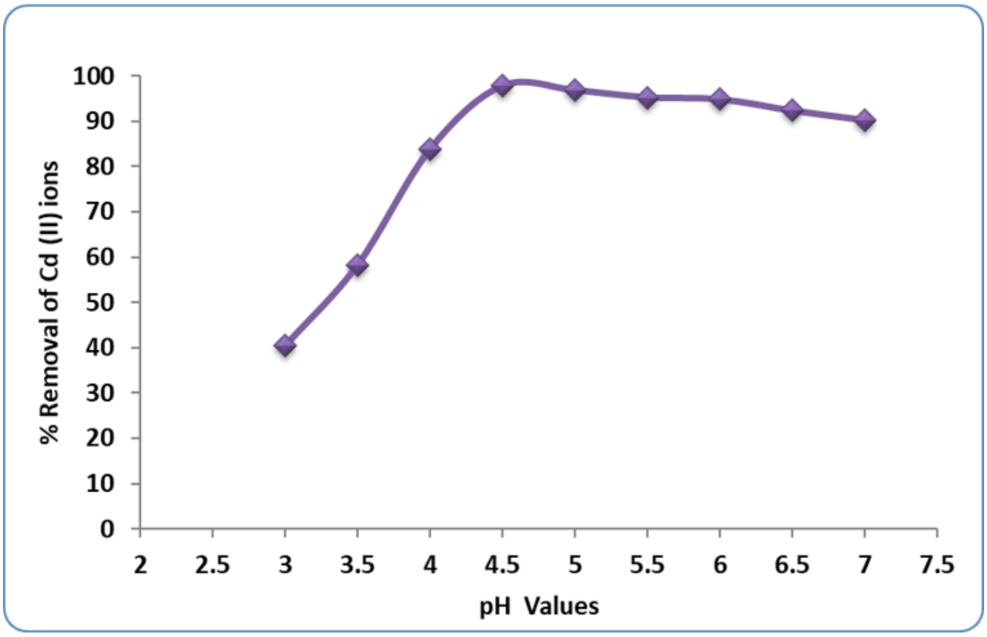

Figure 1: Effect of pH (C_o = 100 mg/L, AIBC = 3.0g/100 mL at 30 ± 2°C)

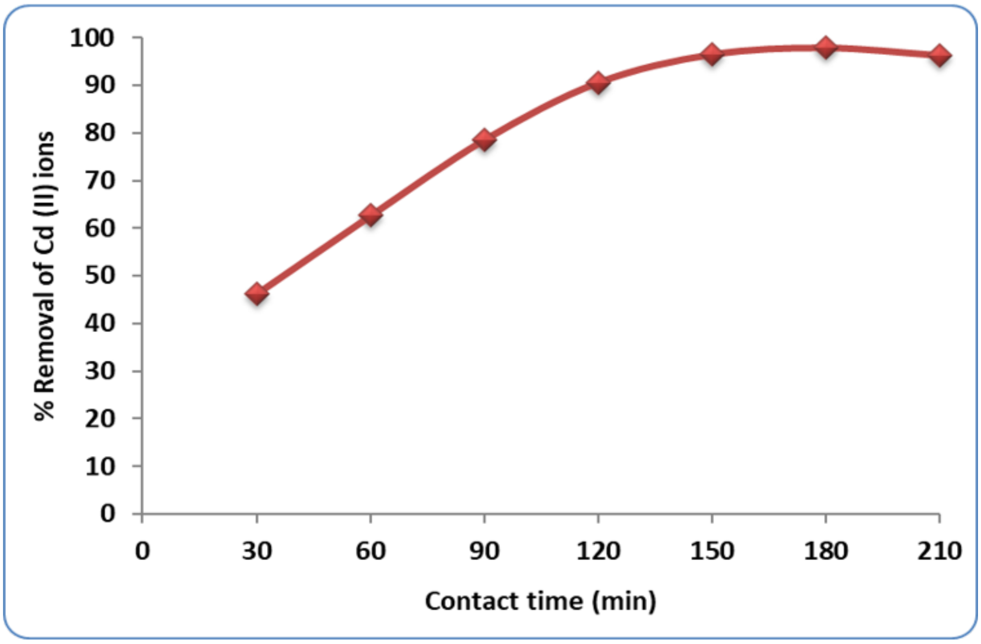

Figure 2: Effect of contact time (C_o = 100 mg/L, pH = 4.5, AIBC = 3.0g/100 mL at 30 ± 2°C)

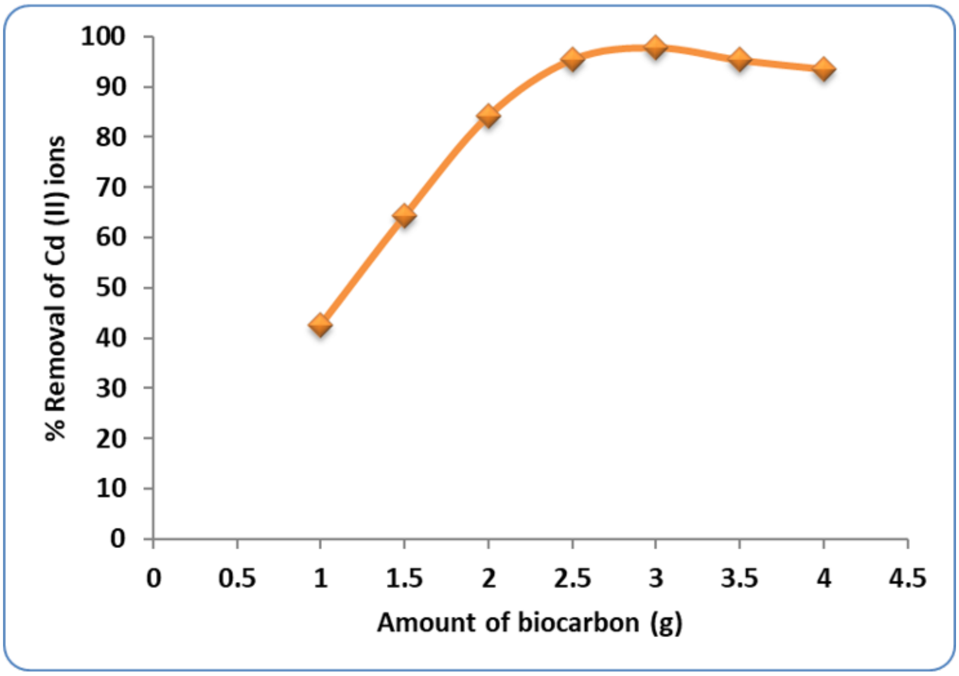

Figure 3: Effect of amount of biocarbon (C_o = 100 mg/L, pH = 4.5 at 30 $\pm$ 2°C)

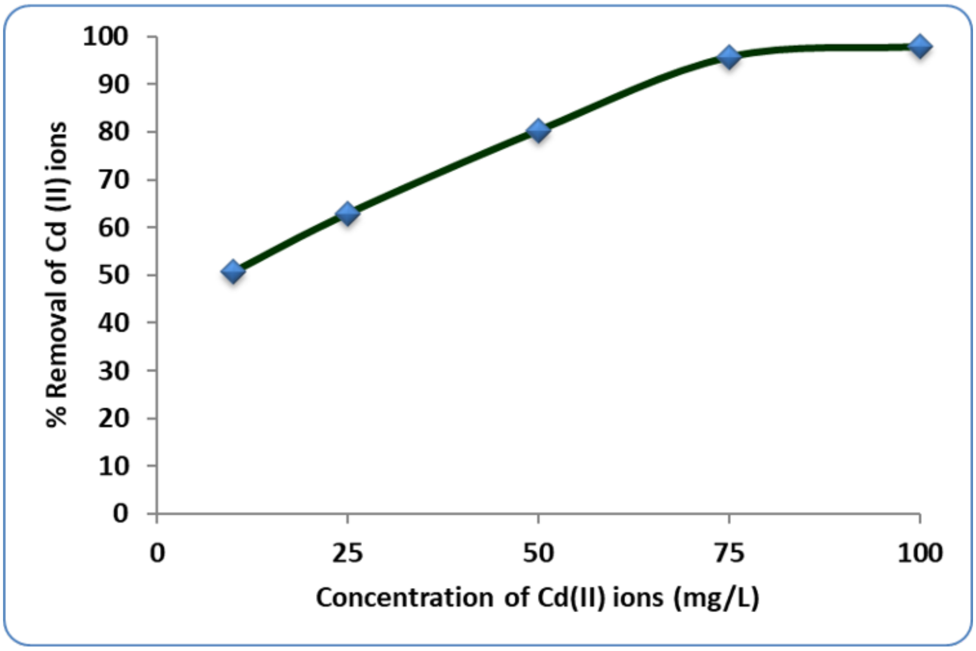

Figure 4: Effect of initial concentration of metal ions (C_o = 100 mg/L, AIBC = 3.0g/100 mL at 30 $\pm$ 2°C)

is due to higher availability of Cd (II) ions in the solution, for the adsorption. This state is often clarified by the fact that there has been a strong possibility of collision at high concentrations between both the adsorbent surface and the metal ions [21].

Effect of temperature

The effect of temperature on the removal of Cd (II) ions efficiency was investigated at constant operating parameters by varying the temperature from 30 ^{o}C to 80 ^{o}C. The temperature has key effects on the adsorption process. It accelerates the diffusion rate of the adsorbate ions into the external boundary layer and within the pores. Additionally, changing the temperature will modify the equilibrium capacity of the adsorbent. The level of cadmium ion removed from stimulated wastewater at different temperatures is shown in Figure 5. The removal of metal ions has been observed to increase significantly while the temperature has risen. This may be due to increased mobility and the spread

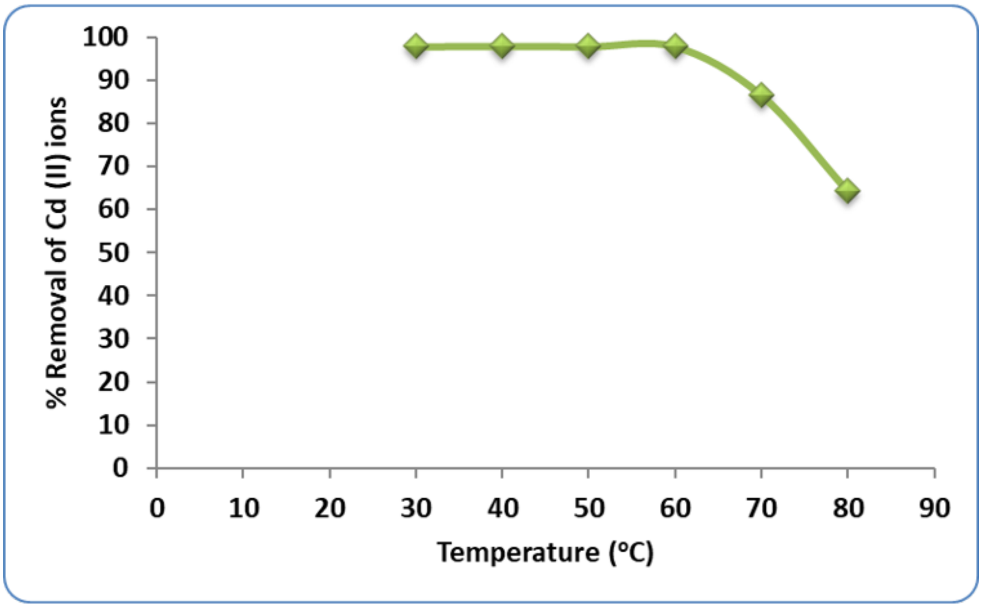

Figure 5: Effect of temperature (C_o = 100 mg/L, pH = 4.5, AIBC = 3.0g/100 mL)

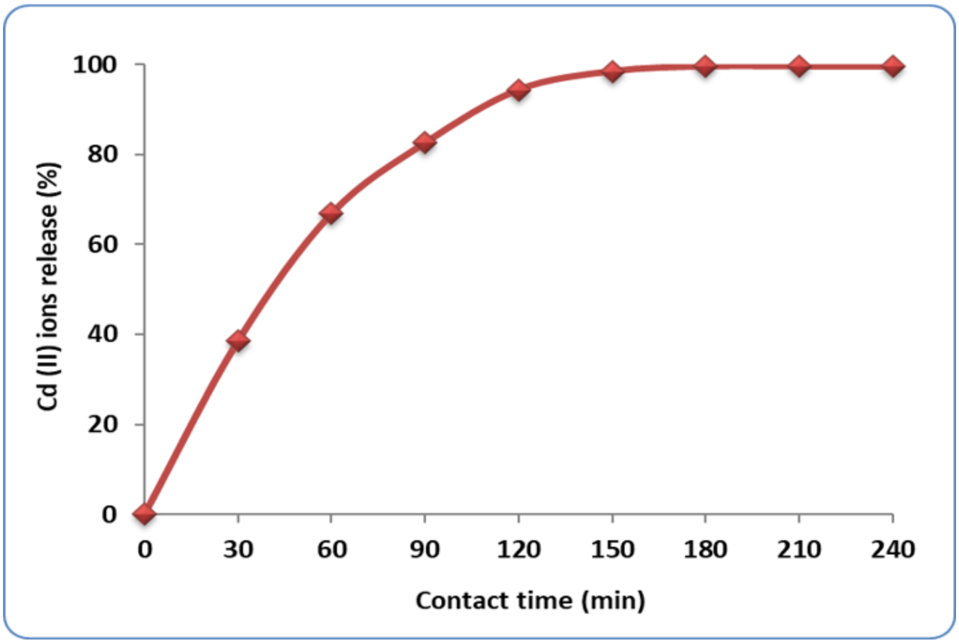

Figure 6: Desorption of Cd (II) ions (pH = 7.8 – 8.35. BCD = 3.0g/100 mL at 30 ± 2°C)

of ion species. It is also well established that diffusion is an endothermal process [16]. The findings suggest that, in addition to physical sorption, the adsorption mechanism of Cd (II) ion on the biocarbon surface could be chemical sorption.

Treatment of industrial wastewater

The use of biocarbon in water and wastewater treatment is very important. Biocarbon materials are therefore tested for the elimination of Cd (II) ions in the selected metal plating industrial wastewater. The pH of the wastewater sample was kept at 4.5 for the efficient removal of metal ions and other pollutants. The wastewater sample is subjected to the treatment process with predetermined equilibrium data. The contact time was 3hrs, the adsorbent dose was 3.0 g and also the agitation speed was 250 rpm. The experimental results of electroplating industrial wastewater were presented in Table 2.

The findings suggest that the disposal of Cd (II) in industrial wastewater is considerably better ($p<0,05$). In addition, the results suggest that 95.16 percent Cd metal ions had been separated from the wastewater by adding only 3.0 g of the adsorbent. The results were also in good agreement with the results of the batch experiments conducted for the removal of Cd (II) in aqueous solution.

Table 2: The results of treatment of metal plating industrial wastewater

Wastewater quality parameters (mg/L)	Results (mg/L)	
	Before treatment	After treatment
pH	4.50 ± 0.2	5.6 ± 0.3
Electrical conductivity (μmhos/cm)	4750 ± 1.5	950 ± 1.2
Total dissolved solids	3095 ± 1.2	620 ± 1.1
Turbidity (NTU)	1.25 ± 0.8	0.2 ± 0.7
Chloride	475.62 ± 1.6	125 ± 1.3
Sulphate	1150 ± 1.8	240 ± 1.5
Calcium	85.54 ± 0.8	12 ± 0.6
Sodium	160.34 ± 0.7	28 ± 0.5
Potassium	46.43 ± 0.9	8.5 ± 0.6
Iron	30.53 ± 1.1	3.6 ± 0.8
Cadmium	45.50 ± 0.8	2.2 ± 0.3
Lead	25.52 ± 0.5	2.5 ± 0.6

Desorption of Cd (II) from AIBC

Disposal of the exhausted adsorbent is also a challenging environmental problem may lead to hazardous pollution problems. The saturated adsorbent which contains significant amount of Cd (II) ions is not safe for disposal due to the stringent environmental constraints. Hence, finding a suitable metal recovery process will help greatly to solve this type of waste disposal problems. Adsorption of any solute on adsorbent takes place by physical bonding, ion-exchange, or a combination of both. In the present study, the desorption of Cd (II) ion was carried out 1.0 N HCl as eluent. In the desorption studies, 98.50 percent of metal ions were recovered at a pH of 7.8 and removed completely at 8.5. The result is shown in Figure 6. Even though, the desorption of metal pollutants from the adsorbent matrix is not an easy task. This seems to be mainly due to the high adsorption capacity of the adsorbent. The effect of microporous regulation is largely due to presence of microporous filling to cause de-sorption lag [22]. Furthermore, it was absolutely difficult to recover the metal ions from the micropore structure of the adsorbent. It is extremely difficult to restore the deformed micropores to the original form, which means that some of the Cd (II) ions could not be released from the adsorbent matrix [23, 24].

CONCLUSIONS

The disposal of Cd (II) ions in metal plating of industry and in stimulated wastewaters using biocarbon technology has been studied in batch experiments. On the basis of the results, the following conclusions can be drawn;

1. AIBC is an efficient adsorbent material for the removal of cadmium ions from industrial wastewater.
2. The adsorption of metal ions increased with the increase in the initial concentration of Cd (II) ions.
3. The maximum percent removal of Cd (II) ions in stimulated wastewater (97.85) and in metal plating industrial wastewater (95.16) was observed by using 3.0 g of adsorbent and the contact time of 180 min.
4. During the desorption studies, a complete metal recovery was observed at the pH of 8.5.
5. This methodology has been applied successfully to the removal of toxic metals from hazardous wastewater.
6. The adsorption methodology is very simple, easy to operate, economically feasible and particularly eco-friendly in nature.

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COMPETING INTERESTS

The authors declare that they have no conflict of interest for this study.

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