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ORIGINAL ARTICLE

A Study on the Adsorption of Cadmium(II) from Aqueous Solution onto Activated Carbon Originated from *Bombax ceiba* Fruit Shell

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KEYWORDS

Adsorption;
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ABSTRACT: Under the present study, the adsorption capability of the activated carbon originated from *Bombax ceiba* fruit shell was examined using batch experimental mode. *Bombax ceiba* fruit shell was carbonized and chemically activated using zinc chloride ($ZnCl_2$) as activating agent. The surface structure of the prepared activated carbon was examined by using scanning electron microscope (SEM). Some important experimental parameters namely pH of the solution, contact time and initial metal ion concentration in the solution, which affect the adsorption process were optimized. Maximum cadmium(II) removal from the aqueous solution was found at pH 9 with 0.3g/30mL adsorbent dose. The equilibrium in adsorption was attained after about 90 min of contact. Different adsorption isotherm models namely Langmuir, Freundlich and Temkin adsorption isotherm models were fitted to explain the equilibrium data obtained for the adsorption system. Temkin isotherm was found to show stronger correlation for cadmium(II) adsorption from the experimental solution onto the prepared adsorbent surface.

INTRODUCTION

Cadmium(II) is one of the major toxic heavy metals found to cause renal disorder, kidney damage, bone fraction, red blood cells destruction and high blood pressure[1]. The main pathway of Cd(II) contamination into the water streams is different industrial processes including mainly electroplating, metallurgical processes, manufacturing of plastics, pigment industries and Cd/Ni batteries[2]. Some conventional process namely chemical oxidation-reduction, adsorption, precipitation, reverse osmosis and electrolytic removal are extensively used to dispel or sequester cadmium from contaminated water[3]. Heavy metal adsorption onto the activated carbon surface has been practiced worldwide. But for developing countries it is difficult to use commercial activated carbon in massive scale because of its high price[4]. Many studies have been conducted with an aim to develop a low-cost activated carbon mainly from different agricultural byproducts, such as bagasse and rice husk[5], corn cob[6], nutshells[7], wood sawdust[8], jackfruit peel[9], rice husks[10], etc. In the present work, the extent of Cd^{2+} adsorption from aqueous solution was studied using activated carbon as adsorbent prepared from *Bombax ceiba* fruit shell. *Bombax ceiba* is a tropical tree, which is usually known as Shimul in Bangladesh. Its fruit is one of the best sources of cotton while the shell is generated as a byproduct, which has no significant use and economical value. Under this study, the

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influence of the experimental solution's pH, contact time and initial Cd(II) concentration in the experimental solution upon the cadmium adsorption with prepared activated carbon was examined. Langmuir, Freundlich and Temkin isotherm models were utilized to explain the equilibrium data.

MATERIALS AND METHODS

Chemicals

Under this study $ZnCl_2$, HCl, NaCl and NH_3 solution were purchased from Merck Life Science Pvt. Ltd. (India) and NaOH pellets and $3CdSO_4.8H_2O$ was taken from Loba Chemie Pvt. Ltd. (India). All of these analytical grade chemicals were used without any further purification.

Preparation of adsorbent

Bombax ceiba fruit shell was collected from Satkhira, Bangladesh. The fruit shells were washed several times with tap water and subsequently distilled water for eliminating possible sands and dirts. The washed shells were dried in sun light for 2-4 days and the dry shells were crushed. The crushed dry shells were soaked well in an activating agent, $ZnCl_2$ (1M).Then the carbonization of the moist sample was carried out in a muffle furnace (FTMF-705, SCI FINETECH, Korea) at 300^oC temperature for 1.5 h. The activated carbonized sample was again soaked with HCl (0.1 M), NaOH (0.1 M) and NH_3 solution. The moist sample was then heated in muffle furnace at 500^oC for 45 minutes in order to increase the porosity of the activated carbonized sample. The resultant activated carbon was washed with distilled water until the pH of the washed solution fell within 6-7 and then dried in an oven at 110^oC temperature for about 2 h. Finally the dried activated carbon was stored in a tightly closed dry container[11,12].

Characterization of adsorbent

The surface structure of the prepared activated carbon was analyzed using scanning electron microscope (SEM)(Hitachi SU-70). And the point of zero charge (PZC) was measured following salt addition method[13]. 0.1 M aqueous solution of NaCl was used as background electrolyte. A series of 30 mL 0.1 M NaCl solutions were taken in different flask and pH was adjusted from 3.0 to 10.0 by the addition of 0.1 M HCl and NaOH solution. A constant weight, 0.3 g of the prepared adsorbent was added to each of those solutions. All of the suspensions were shacked manually and kept for 48 h with intermittent shaking. After 48 h, the change in pH (ΔpH) of those solutions was recorded by the same pH meter (pH5011, Ezdo, Taiwan). These measured ΔpH was plotted against initial pH and PZC was revealed by the pH at which ΔpH=0 on this graph.

Preparation of aqueous cadmium(II) solution

Stock solution of cadmium(II) was prepared through dissolving 2.3049 g of $3CdSO_4.8H_2O$ in 1000 mL of deionized water; 1.00 mL=1.00 mg cadmium(II). The other required experimental solutions of different concentrations were prepared by serial dilutions of the prepared stock solution.

Batch experimental program

The extent of cadmium(II) adsorption onto the prepared activated carbon was examined using batch experimental mode which was performed through mixing of 0.3 g adsorbent with a fixed volume (30 mL) of cadmium(II) solution at room temperature. The mixture was agitated at 150 rpm in orbital shaker (SK-0180-S, Scilogex, India). After a certain contact time, the mixture was centrifuged with a centrifugal machine (LC-8, Benchmark Scientific, USA) for 5 min and filtered using Whatman-42 filter paper. The remaining Cd(II) concentration in the filtrate was examined by an atomic adsorption spectrophotometer (AAS) (Shimadzu AA-7000, Japan). For optimization of some important parameters namely pH of the experimental solution, contact time and initial Cd(II) concentration, the batch experiments were conducted at different pH (4, 5, 6, 7, 8, 9 and 10), contact time (15, 30, 60, 90, 120, 150 and 180 min) and initial Cd(II) concentration (5, 10, 15, 20, 25 and 30 $mg.L^{-1}$) respectively. The removal percentage (%R)

of cadmium(II) was calculated using the following relationship:

$$\%R = \frac{C_i - C_f}{C_i} \times 100$$

Where C_i and C_f are the initial and final cadmium(II) concentrations in mg.L^{-1} respectively. The amount of cadmium(II) adsorbed per unit weight of adsorbent in mg/g was calculated using the following relationship:

$$Q_e = \frac{C_o - C_e}{W} \times V$$

Where C_o and C_e are the initial and equilibrium cadmium(II) concentration in mg.L^{-1} respectively, V is the volume of the solution in L and W is the mass of the adsorbent in g.

RESULTS AND DISCUSSION

Characterization of adsorbent

Point zero charge (PZC) of the prepared activated carbon was determined 6.7 (Figure 1). Below this pH the surface becomes positively charged because of the protonation of the functional group, which facilitates anion adsorption on the surface due to electrostatic attraction between the opposite charges. Similarly above this pH the surface becomes negatively charged and facilitates cation adsorption[14].

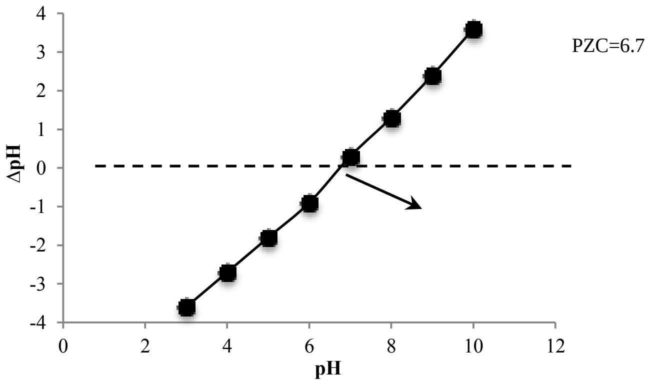

Figure 1. Point zero charge (PZC) of activated carbon originated from *Bombax ceiba* fruit shell

SEM image of the prepared activated carbon is shown in Figure 2. This image indicates the porous structure of the activated carbon that could attribute to cadmium(II) adsorption.

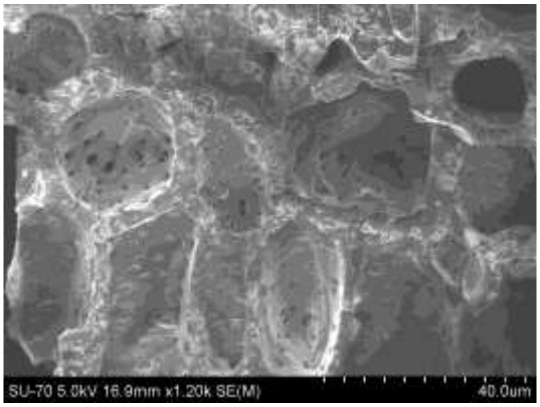

Figure 2. SEM image of activated carbon originated from *Bombax ceiba* fruit shell

Effect of pH

The initial pH of the experimental solution is counted as very important factor influencing the extent of metal adsorption. pH of the experimental solution influences the availability of metal ions and as well as the charges of the adsorbent surface. The optimization of pH was carried out by varying the solution pH from 4 to10 for 30 mL of 15 mg.L^{-1} Cd(II) concentration, 0.3 g of adsorbent dose and 120 min of contact time. Cd^{2+}adsorption was increased with the increasing of solution pH and becomes maximum (78.73%) at pH 9 after which the adsorption was again started to show decreasing trend which is represented in Figure 3.This finding can be confirmed on the basis of PZC which is estimated 6.7 for the prepared activated carbon. At pH lower than 6.7 the adsorbent surface becomes positively charged which inhibits the adsorption of positively charged Cd^{2+} ions because of electrostatic repulsion and at pH higher than 6.7 the adsorbent surface becomes negatively charged which facilitates the adsorption of Cd^{2+} through electrostatic attraction. Again the low level of Cd^{2+}adsorption at lower pH could also be attributed to the increased hydrogen (H^+) ions concentration in the solution, which compete with Cd^{2+} ions for binding sites. And after pH 9 the cadmium ion forms $Cd(OH)_2$ which decreases the removal efficiency[4,15].

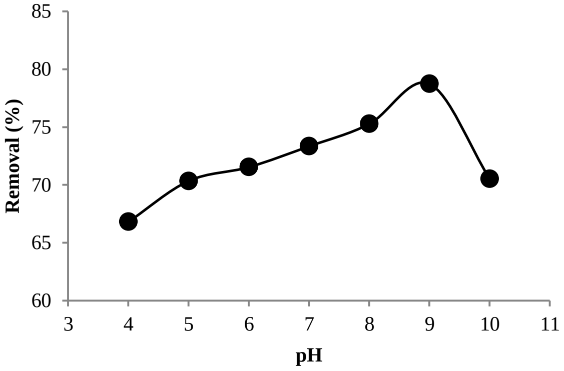

Figure 3. Effect of pH on Cd(II) adsorption onto activated carbon originated from *Bombax ceiba* fruit shell

Effect of contact time

The optimization of contact time was performed by varying the contact time 15, 30, 60, 90, 120, 150 and 180 min for the treatment of 30 mL 15 mg.L^{-1} Cd(II) solution with 0.3 g of adsorbent at pH 9. The result revealed that at first 90 minutes of the adsorption increased significantly with contact time, after that the adsorption seems to reach equilibrium, which is shown in Figure 4. This is because of high Cd(II) ion concentration in the experimental solution and as well as available vacant active sites on the adsorbent surface initially. After the equilibrium point the available vacant active sites on the adsorbent surface decreased significantly and thus the metal removal rate slows down[16].

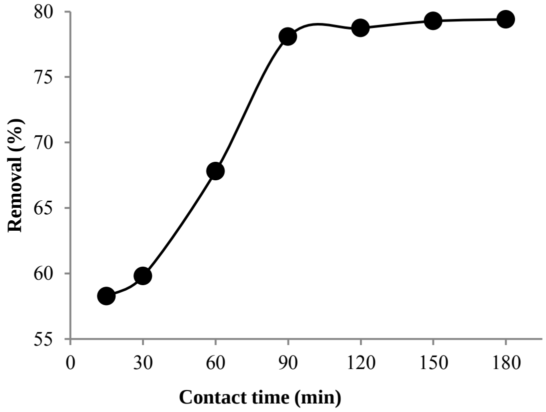

Figure 4. Effect of contact time on Cd(II) adsorption onto activated carbon originated from *Bombax ceiba* fruit shell

Effect of initial cadmium(II) concentration

The initial metal ion concentration in the solution is also another important factor affecting the metal adsorption on the adsorbent surface. It is a driving force to overcome the resistance of mass transfer of all metal ions between solid and aqueous phases[17]. The optimization of initial cadmium(II) concentration was performed by varying the initial cadmium(II) concentrations (5, 10, 15, 20, 25 and 30 mg.L^{-1}) in 30 mL solution which was treated with 0.3 g of prepared adsorbent at pH 9 for 120 min. It was observed that initially cadmium(II) adsorption onto the prepared adsorbent surface was increased with the increasing of initial cadmium(II) concentration in the experimental solution and become maximum (79.35%) at 20 mg.L^{-1} of cadmium(II) concentration and then the adsorption was again started to decrease which is represented in Figure 5. Before achieving maximum removal at 20 mg.L^{-1} of initial cadmium(II) concentration, the increasing trend of metal adsorption could be imputed to the fact that the higher initial metal ion concentrations boost up the adsorption process[16]. After achieving maximum removal at 20 mg.L^{-1} of initial cadmium(II) concentration, the decreasing trend of metal adsorption could be because of increased metal ion concentration for the same active sites resulting overloading on the active sites of the adsorbent surface[18].

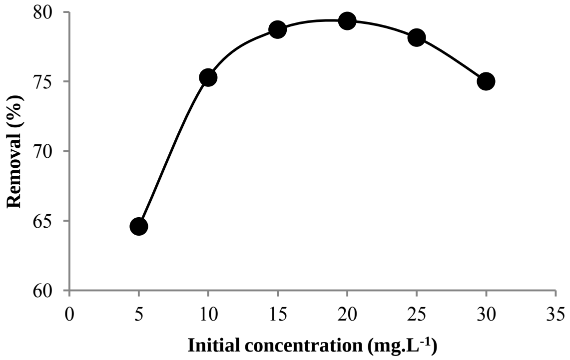

Figure 5. Effect of initial metal ion concentration on Cd(II) adsorption onto activated carbon originated from *Bombax ceiba* fruit shell

Adsorption studies with various isotherm models

Cadmium(II) adsorption onto the activated carbon originated from the *Bombax ceiba* fruit shell was investigated with the Langmuir, Freundlich and Temkin model. The Langmuir model states that the adsorbent surface is perfectly homogeneous, all sites are energetically identical and only monolayer can be formed [19]. The linear form of the model is given by:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \ldots\ldots\ldots (1)$$

Here, C_e is the equilibrium concentration of the solute, Q_e is the amount of adsorbed solute at equilibrium, Q_m is the maximum possible amount of adsorbed solute and K_L is the equilibrium constant of adsorption.

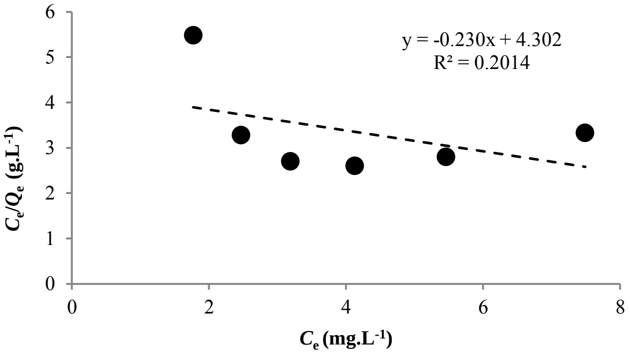

Figure 6. Langmuir isotherm for Cd(II) adsorption onto activated carbon originated from *Bombax ceiba* fruit shell

With the adsorption data of the present study, a linear plot (Figure 6) of equation 1 gives Q_m and K_L with the coefficient of correlation, $R^2 = 0.201$ suggesting that the adsorption does not agrees with the assumptions of Langmuir model. In fact, from the SEM image it is clear that the adsorbent surface is not even physically homogeneous, which is the major assumption of Langmuir isotherm. However, the Freundlich model assumes that the amount adsorbed is proportional to the solute concentration raised by the power of $1/n$. The model also predicts a heterogeneous adsorption. The linear form of Freundlich model is given by-

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \ldots\ldots\ldots (2)$$

Here, n indicates how favorable the adsorption process is and K_f signifies adsorption capacity of the adsorbent.The adsorption is described as normal when $1/n < 1$ and cooperative when $1/n > 1$[20].

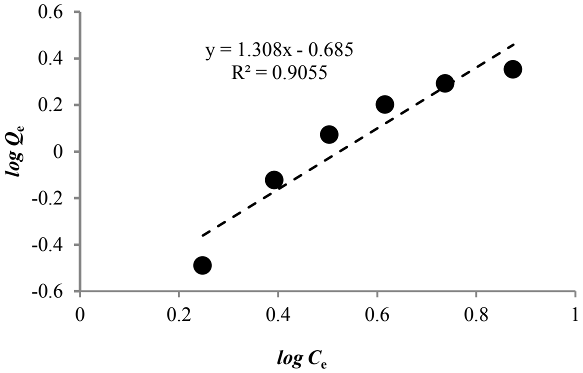

Figure 7. Freundlich isotherm for Cd(II) adsorption onto activated carbon originated from *Bombax ceiba* fruit shell

The linear plot (Figure7) of equation 2 with the experiment data gives the K_f and n with the coefficient of correlation, R^2= 0.9055. The R^2 value closer to unity indicates that the surface of the activated carbon prepared from *Bombax ceiba* fruit shell is physically and energetically heterogeneous. Hence, acomprehensible insight can be obtained by fitting the experiment data with the Temkin model:

$$Q_e = \frac{RT}{B}\ln K_T + \frac{RT}{B}\ln C_e \ldots\ldots\ldots(3)$$

The Temkin model usually signifies heterogeneous surface energy systems (non-uniform distribution of the heat of sorption). The constant B relates to the sorption heat, $B \approx q = -\Delta H$. K_T is the equilibrium binding constant corresponding to the maximum binding energy.

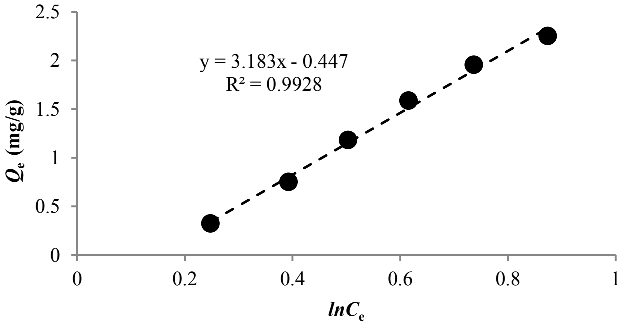

Figure 8. Temkin isotherm for Cd(II) adsorption onto activated carbon originated from *Bombax ceiba* fruit shell

The liner plot (Figure 8) of equation 3 with the corresponding experiment data gives the value of B and K_T with the coefficient of correlation, R^2=0.993, which significantly correlate the theory and experiment data.

All the parameters obtained from different adsorption models are listed in table1. $1/n$=1.308 indicates that the adsorption is cooperative and the adsorbent facilitates weak adsorption of cadmium(II) onto its surface. Positive value of B means the adsorption process in the present study is exothermic.

Table 1. Parameters obtained from different adsorption models.

Langmuir model	**Freundlich model**	**Temkin model**
Q_m= 4.37	K_f= 4.84	B=0.13
K_L= 0.053	$1/n$ = 1.308, n = 0.76	K_T= 0.87
R^2 = 0.201	R^2 = 0.905	R^2 = 0.993

Cost-benefit analysis

Different authors produced single walled and multi walled carbon nano tubes for wastewater treatment with the average price of 45,000–140,000 $/kg and 1500–10,000$/kg respectively[21,22]. Wang *et. al.* showed that the production of ion exchange resin may spend up to 150 $/kg[23]. In comparison, activated carbons can be attainable at a mentionable lower price ranging from 2 to 5 $/kg[24, 25]. In most cases the production cost involves the preparation process of adsorbent and purchasing required reagents, where the cost of raw material is comparatively very low or sometimes even negligible depending on its source. The production of activated carbon from from *Bombax ceiba* fruit shell using different reagents and equipments costs approximately 3.0 to 4.5 $/kg, which is much beneficial compared to other adsorbents like carbon nano tube and ion exchange resin.

Comparison analysis with other studies

A survey revealed that Mohanty *et. al.* removed phenol using nutshell with the maximum adsorption of 11.16 mg/g[7]. When papaya wood[26] is used to remove Cd(II), the maximum adsorption was identified to be 9.33 mg/g. Tran *et. al.* used sugercan baggasse and removed Ni(II), Cu(II) and Pb(II) with maximum adsorption of 2.99 mg/g, 13.24 mg/g and 19.3 mg/g respectively[27]. Orange peel powder, also a naturally found adsorbent can remove Cd(II) up to 76.6 mg/g[28]. In our study, the Cd(II) adsorption on activated carbon prepared from *Bombax ceiba* fruit shell, the maximum adsorption was ascertained to be 3.94 mg/g.

CONCLUSIONS

The extent of adsorption efficiency of the activated carbon originated from *Bombax ceiba* fruit shell was identified to be dependent on the solution pH, contact time and initial metal ion concentrations. The activated carbon was originated from *Bombax ceiba* fruit shell through carbonization followed by chemical activation with activating agent, $ZnCl_2$.Under the characterization of the prepared adsorbent, its surface was found to be porous in SEM image and point zero charge was determined 6.7. The optimization of different experimental parameters through batch experimental mode identifies the optimum pH: 9, contact time: 90 min and initial Cd(II) ion concentration: 20 $mg.L^{-1}$ with 0.3 g/30 mL adsorbent dose. Temkin isotherm was found to provide stronger correlation with the experiment data. The adsorption of Cd(II) onto the activated carbon obtained from *Bombax ceiba* fruit shell was found to be weak and cooperative, where the process is exothermic.

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Conflict of interest

The authors declare no conflict of interest.

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