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Biosorption of Cadmium from Solution by *Trapa nantas*

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ABSTRACT

Biosorption of Cd(II) is an effective technology for the treatment of industrial wastewater. In the present research article, generation of activated carbon derived from fruit shell of Trapa nantas, followed by its characterization using modern techniques like FTIR SEM, XRD and TGA studies have been reported. Different physical properties such as Particle size, Bulk Density, Moisture content, Water Soluble Matter and Acid Soluble Matter were also determined. This newly obtained activated carbon has been tested to estimate its practical applicability for removal of Cd(II) from aqueous solution. Adsorption capacity of Trapa Nantas Fruit Shell Activated Carbon (TNFSAC) for Cd(II) abetment was investigated employing batch equilibration method.. The influence of pH, contact time, adsorbent doses and initial Cd(II) concentration have also been studied and reported. UV-Visible spectrophotometer was used to determine the concentration of aqueous Cd(II) during the experiments. The results revealed that the activated carbon adsorbent reported in this article is effective for removal of Cd(II) from wastewater and thus can be successfully used for control of cadmium pollution.

Keywords: *Cdmium, XRD, trapa nantas and pollution*.

INTRODUCTION

At the present, national development and agricultural productivity in India is heavily dependent on natural rainfall which result droughts in various parts of our country during the last decade. With the increase in age of the earth, clean water is becoming more precious as water being polluted by several man made activities, e.g. rapid population growth, alarming speed of industrialization and deforestation, urbanizations, improving living standards and wide spheres of other human activities. Water pollution is the contamination of water bodies eg. lake, river, oceans, aquifers resulted due to discharge of pollutants into water bodies without adequate pretreatment to remove harmful components. In almost all cases, the effect is damaging not only to individual species but also the natural biological communities. Cadmium is one of the most toxic environmental and industrial pollutant because it can damage almost all important organs [1]. Cadmium alloys and its compounds are used in a variety of consumer and industrial materials [2-5]. Even small quantity of Cd assimilation by the body can cause severe high blood pressure, heart disease and can lead to death [6]**.** The commonly used methods for removing metal ions from waste water include precipitation, lime-coagulation, reduction, electrolytic removal, ion-exchange, reverse osmosis, membrane filtration and solvent extraction[7-12]. Bio-sorption a technically feasible and economical process, has gained increased creditability during recent years [13]. A number of biosorbents have been used such as tree barks, saw dusts, activated rice husk, coconut shell, almond shell etc. for the adsorption of heavy metals. Use of surface modified/chitosan coated bio-sorbent as low cost material for abatement of Cr(VI) has been reported in the literature[14]. Therefore, attempt has been made to synthesize the new activated carbon from *trapa nantas* and study its properties with special reference to Cd(II) abatement.

MATERIALS AND METHODS

All the chemicals used were of analytical or chemically pure grade. Distilled water was used throughout the investigation.

Biomass

Fruit shell of *trapa nantas* was collected as waste and washed several times with tap water followed by distilled water. The clean biomass so obtained was oven dried at 130^{0}C for 24hrs. The dry biomass was milled and sieved to get fine particles.

Preparation of activated carbon

The biomass was subjected to pyrolysis process using Muffle Furness. During slow carbonization of raw material in the absence of air at temperature range700-800^{0}C, volatile product was removed and residue was converted into char. The char was then subjected to chemical activation process using 25% zinc chloride solution. The material has been characterized by FTIR, XRD, TGA and SEM studies. The adsorbent material obtained has been abbreviated as TNFSAC.

Characterization of Activated Carbon Powder

Particle size

Particle size determination is one of the most important aspects during the characterization of any adsorbent. It generally affects adsorption rate but not the adsorption capacity. The determination of particle size was mode by keeping a fixed weight of the products on a set of sieves placed on a shaking device. The material retained on each sieve was weighted and form the data obtained, the particle size for each adsorbent has been determined employing the standard procedure [15].

Bulk Density

For the determination of bulk density, a trip balance was used to fill the materials in the graduated cylinder. Initially, 100 ml graduated cylinder was accurately weighed. Sufficient amount of the material was transferred to the cylinder with constant tapping and allowed it to fill up to 50 ml mark. The shaker attached to the balance is adjusted in such a way that the material gets filled into the graduated cylinder at rate of 1ml approximately per second. After filling the graduated cylinder with the carbon material, it was again weighed accurately. The bulk density was calculated from the weight of carbon material and volume occupied by it.

Moisture content

About one gram of the powdered air dried activated carbon powder was taken in a previously weighed crucible. The crucible was placed in an electric hot air oven maintained at about 110^{0} C. After one hour the crucible is taken out, cooled in a desiccator and weighed again. The loss in weight of the powder reported on percentage basis gives moisture content in the sample.

Water Soluble Matter

10 gm of the carbon material of known moisture content was weighed accurately and transferred into a one lit beaker. About 300 ml of double distilled water was added into it and heated to boiling with continuous stirring and stirring was continued for 5 minutes. The material was then allowed to settle and the supernatant liquid was filtered through a gooch crucible fitted with on asbestos mat. The procedure was repeated thrice with the residue in the beaker using 300 ml of double distilled water each time. The combined filtrate was concentrated to less than 100ml over a water bath, cooled and the volume was made up to 100 ml mark in a volumetric flask. Exactly 50ml of the filtrate was transferred to a china dish, evaporated to dryness on hot plate, it was dried in hot air oven at 110 ± 5°C and cooled in a desiccators and accurately weighed. The procedure of drying and weighing was repeated at intervals of 30 minute until the difference between two consecutive weighing was less than 5 mg. The percentage of water soluble matter has been calculated using the following formula,

$$\text{Water soluble matter }(\%) = \frac{M\, x\, 100}{\frac{M_1}{100}\,(100 - Y)}$$

Where M is mass of the residue in grams
M_1 is mass of the material taken for test in grams
Y is percentage of moisture present in the material

Acid Soluble Matter

10 gram of the carbon material under study was weighed accurately and transferred into one lit. beaker. 300 ml of 0.25N HCl solution was added and heated to boiling with continuous stirring for about 10 minutes. After cooling the insoluble part is washed, weighed and acid soluble matter is calculated.

Preparation of Cd (II) solution

A Cd(II) stock solution having 500mgl^{-1} concentration was prepared by dissolving 0.2854g of cadmium sulphate [$3CdSO_4.8H_2O$] in 1000ml of distilled water. This solution was diluted to proper proportions to obtain various standard solutions ranging their concentrations 10-100mgl^{-1}. pH adjustment was done using 0.5N HCl and 0.5N NaOH solution.

Batch Experiment

Batch equilibrium studies were conducted with different parameters such as pH, agitation time, initial concentration Cd(II) solution and effect of adsorbent doses. The systems were agitated on rotary shaker at 200 rpm, filtered through Whatmman no.42 filter paper and filtrates were analyzed for Cd(II) concentration using UV-Visible Spectrophotometer. From experimental data, the applicability of Freundlich isotherm and Langmuir model were judged. Linear regression coefficient (R^2) and isotherm constant values were determined from these models.

RESULT AND DISCUSSION

FTIR Studies of TNFSAC

FTIR spectrum of TNAC has shown in **Fig.1**. The peaks in range 3500-3860 cm^{-1} indicate N-H stretching. The weak peaks appeared in range 1600cm^{-1} to 1750cm^{-1} indicate the presence C=O stretching in carboxylic acid. The peaks appeared in range 1500cm^{-1} to 1580cm^{-1} indicate the presence of C=C bond stretching and peak at 1399cm^{-1}indicates N-O asymmetric stretching.

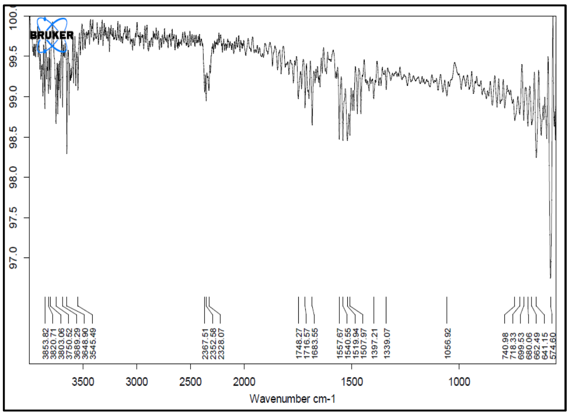

Fig. 1 FTIR Spectrum of TNFSAC

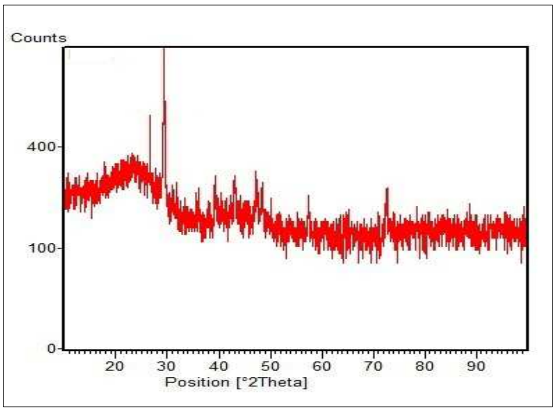

Fig. 2 X-Ray Diffraction Pattern of TNFSAC

XRD pattern of TNFSAC

X-ray diffractograph of *Trapa natus* activated carbon has shown in **Fig. 2**. In this XRD pattern the first peak observed at $2\theta = 28^0$ indicate amorphous nature. The another small peaks are found with low intensity in spectrum suggested that nature of carbon is amorphous.

SEM analysis of TNFSAC

SEM image of TNFSAC has shown in **Fig. 3.** From the SEM image of TNFSAC it is clear that significant numbers of pores are formed during the activation pores of TNFSAC. Thus activation process by using $ZnCl_2$ solution was successful in creating well-developed pores on the surfaces of activated carbon material. The SEM micrograph indicates that the pores are consisting of cylinder like tubes, which would easily capture and retain the metal ions(pollutants) from aqueous solution.

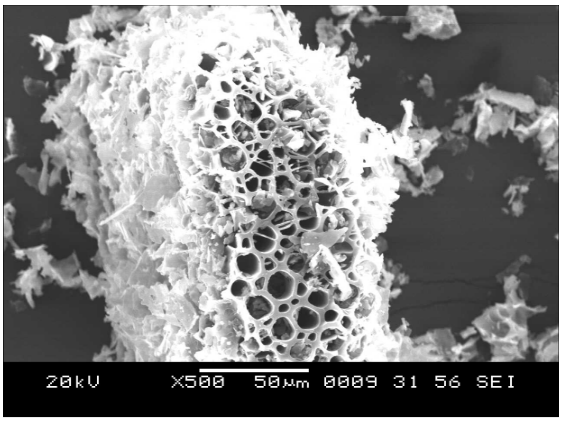

Fig 3 SEM image of TNFSAC

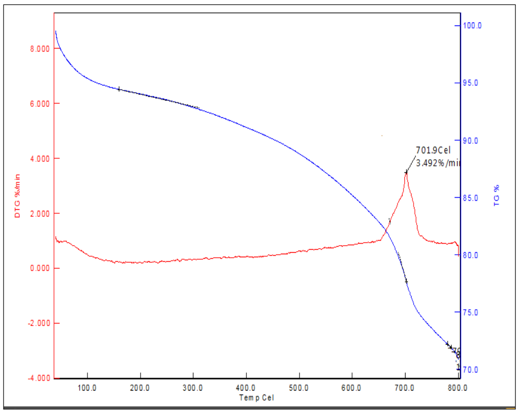

Fig.4 TGA curve of TNFSAC

TGA studies of TNFSAC

T.G curve of TNAC was shown in **Fig 4**. Two decomposition stages can be observed in the thermograph, first at 150^0C and second at 700^0C. The first derivative peak at 150^0C with weight loss 6%. This weight loss of the material may be due to release of some unknown evaporable matter. The second peak observed at 700^0C with weight loss 23% due to the decomposition of other organic molecules.

Studies of physical properties of TNFSAC

The particle size of TNFSAC adsorbent was found to be 0.81 mm which is indicative of the adsorbent having high speed/rate of adsorption. Bulk density may be regarded as the measure of activity for adsorbents. Higher is the bulk density, faster the settling rate and the volume of sludge to be handled and dewatered after treatment will be less. Moisture content does not affect the adsorptive power but dilutes the adsorbent and necessitates the use of additional weight of adsorbent to provide the required weight (dosage). Moisture content noticed in TNFSAC adsorbent under study is found considerably very low. Acid soluble matter is high in TNFSAC. Results of physical properties of TNFSAC obtained have shown in table 1.

Table 1:- Characteristics of TNFSAC adsorbent

Properties	Particle size (mm)	Bulk density (gm/lit)	Moisture content (%)	Water Soluble Matter(%)	Acid Soluble Matter(%)
TNFSAC	0.81	0.246	1.23	0.54	0.91

Adsorption Equilibrium Studies

Effect of pH on adsorption

Effect of pH on Cd(II) adsorption using TNFSAC as an adsorbent has been studied in the pH range 1to10 and presented in Fig.5. It is seen that solution pH plays a very important role in the adsorption of Cd(II). The percentage removal increases steadily from 46 to 87% when pH is increased from 1 to 5 in Cd(II) adsorption and slowly decreases on further increases in pH.

Effect of contact time on adsorption

Adsorption experiments were conducted as a function of contact time and results have shown in Fig.6. The rate of Cd(II) binding with adsorbent was greater in the initial stages then gradually increases and remains almost constant near about 92%, after optimum period of 110 min.

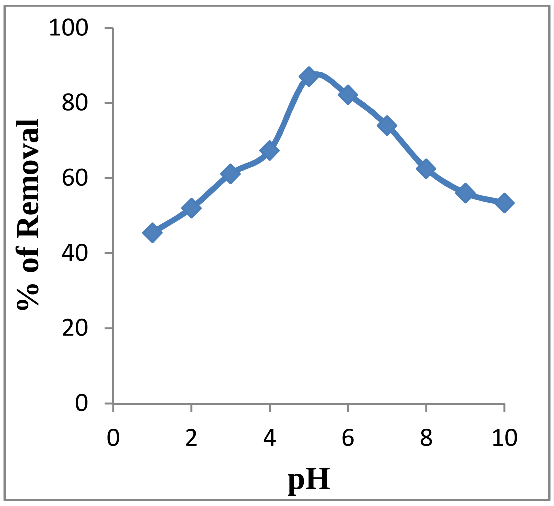

Fig. 5 Effect of pH on Cd(II) removal

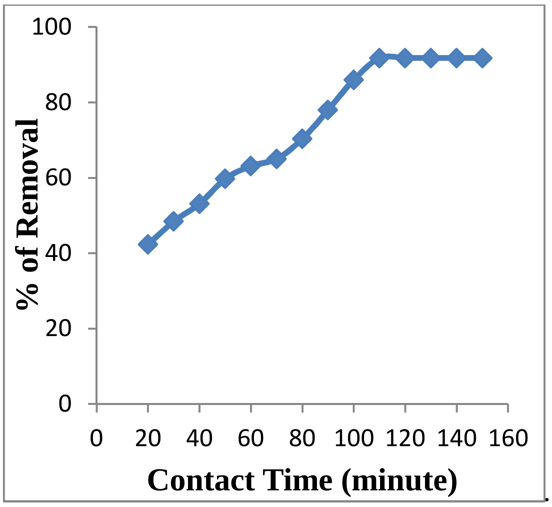

Fig. 6 Effect of Contact time on Cd(II) removal

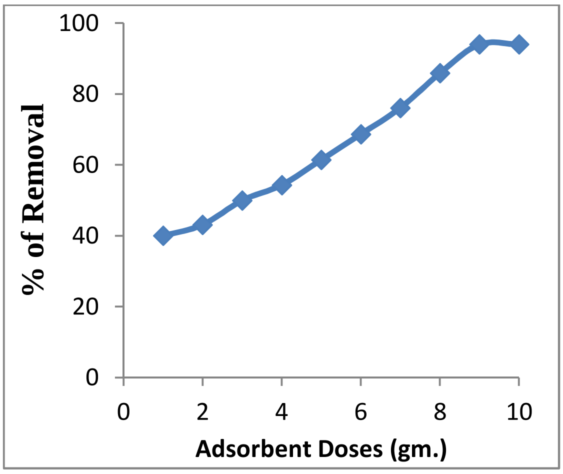

Fig. 7 Effect of Adsorbent doses on Cd(II) removal

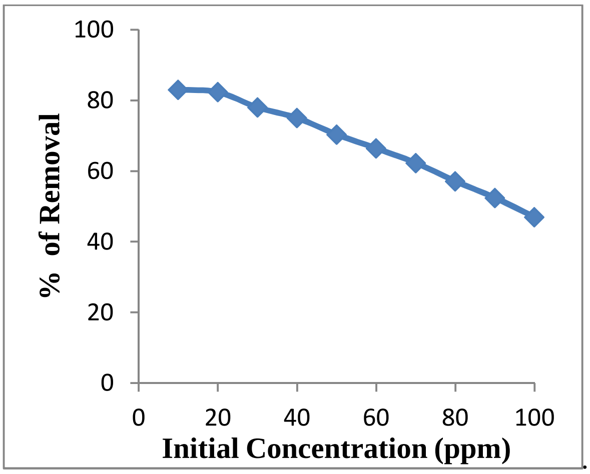

Fig. 8 Effect of initial concentration on Cd(II) removal

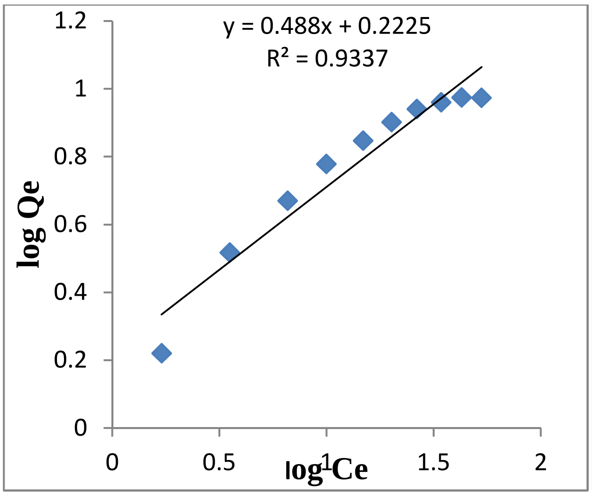

Fig. 9 Freundlich isotherm for the adsorption of Cd(II)

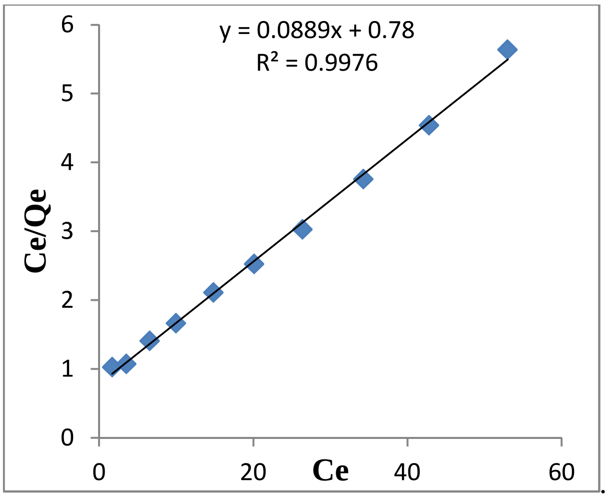

Fig. 10 Langmuir isotherm for the adsorption of Cd (II)

Effect of adsorbent doses

The effect of adsorbent (TNFSAC)doses on percent removal of Cd(II) in the range 1 to 10gm is represented in Fig.7. The initial Cd(II) concentration was taken to be 30ppm. However after certain adsorbent dose it becomes constant and it is treated as an optimum adsorbent dose, which is found to be 9 gm/lit. for the TNFSAC adsorbent.

Effect of the Initial concentration of Cd(II) solution

The Experimental studies were carried with varying initial concentration of Cd(II) ranging from 10 to 100 ppm using 7 gm/lit. of adsorbent dose. The results have shown in Fig.8. The results demonstrate that at a fixed adsorbent dose the percentage of Cd(II) removal decreases with increasing concentration of adsorbate.

Adsorption Isotherm

Freundlich adsorption isotherm

The plot of $\log Q_e$ versus $\log C_e$ for Cd(II) is presented in Fig.9 which show linear curve and hence the adsorption process obeys Freundlich adsorption isotherms. Freundlich constants 'n' and 'k_f' for Cd(II)) were found to be 2.049 and 1.699 mg/g respectively. The square of the correlation coefficient (R^2) values was found to be 0.9337 for Cd(II) which shows well-fitting of the Freundlich isotherm. The 'n' values are in between 1 to 10 which indicate the favorable adsorption of Cd(II) on TNFSAC.

Langmuir adsorption Isotherm

The results obtained from Langmuir model for the removal of Cd(II) by TNFSAC has been represented in Fig.10. The values of square of the correlation coefficient (R^2) is found to be 0.9976 for Cd(II), which show the best fitting of equilibrium data. The values of 'Q_m' for Cd(II) was found to be 11.24 mg/g while values of 'b' was 0.114. The lower values of b(less than one) implies an excellent the affinity between solute and sorbent sites. To confirm the adsorbility of the adsorption process, the equilibrium parameter also called separation factor (R_L) for Cd(II) was calculated which were found to be 0.2248.

CONCLUSION

i) Activated carbon TNFSAC has been obtained and activate successfully.
ii) The activated carbon derived from the Fruit Shell of *trapa nantas* has been characterized by FTIR,XRD,TGA and SEM studies.
iii) TNFSAC was most effective for Cd(II) removal. At pH 5, 87% of Cd(II) was removed from aqueous solution and adsorption was found to be pH dependent.
iv) The increase in percent removal capacity was observed with increased adsorbent doses and contact time. Maximum Cd (II) removal is 94% for 9.0 gm/lit. dose and 92% at 110min. of contact time respectively.
v) The newly obtained activated carbon under present investigation can be successfully employed for Cd(II)abatement from contaminated water and thus can be used for water/ wastewater treatment and pollution control.

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