Prepared Bio-adsorbent (Jackfruit Seed) for Cadmium Removal from Waste Water

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Abstract - In the present study, Jackfruit seed powder (JFSP) was synthesized and utilized as cost effective bio-adsorbent for the removal of cadmium from synthetic wastewater. JFSP was characterized using FE-SEM, EDX, TGA, FTIR, XRD, and ICP techniques. Effects of functional parameters such as solution pH, dosage of adsorbent, stirring speed and concentration of cadmium removal were evaluated and optimized. The maximum adsorption was achieved at speed of 120 rpm, pH 7.6 and contact time of 1 h. Activation energy of the JFSP was also being evaluated, which indicate that cadmium adsorption by JFSP was chemisorptions process.

Keywords: Bio-adsorbent; thermal kinetics; jackfruit seeds; cadmium removal.

I. INTRODUCTION

Chemical industries effluents mostly contain heavy metals such as cadmium, iron, copper, chromium, arsenic, lead etc. and its compounds. These heavy metals may bring long-term threat to environment and human being, when released in water (Kumar et al., 2014). Cadmium (Cd) is considered to be one of the most hazardous contaminants present in waste water. These contaminants generally enter into the water bodies through various industrial and agricultural practices and can adversely reacts with the ecosystem even at very low quantities (Bhanjana et al., 2017; Hashemi et al., 2018) Therefore before discharging the wastewater in the river and lake from these industries, effluent treatment is required. After treatment the maximum limit of cadmium is equals 0.003 mg/L. There are different methodologies available for wastewater treatment like coagulation, electro-coagulation, flocculation, filtration, membrane separation; adsorption reverses osmosis, precipitation and bioremediation. Among them, adsorption is one of the most common and commercially adopted techniques because of its good efficiency with simple procedure and low operational cost (Gupta et al., 2012; Alslaibi et al., 2013; Demirbas, 2008). Due to the high cost of commercial carbons, researchers are searching for the material which is cheap, affordable and easily accessible to produce activated carbon. In this respect, agricultural and industrial wastes can be those appropriate raw materials to produce appropriate activated carbon for the removal of heavy metals from the waste water (Liew et al., 2018; Norouzi et al., 2018; Adebisi et al., 2017).

The present study is focused on the synthesis, characterization, thermal degradation kinetic of biomass to used material like jackfruit seeds (JFS) and its application in cadmium removal from synthetic wastewater.

II. MATERIALS AND METHOD

a. Experimental setup and procedure

A home grown experimental setup has been assembled to perform in batch adsorption process (Pal et al., 2017). The experimental setup consist a magnetic stirrer of capacity 0 to 500 rpm with least count 5 rpm and 100 ml beaker consists of lead contained water with different concentration range varying from 0.5 to 2.5 ppm has been subjected to purify in presence of bio-adsorbent (catalyst). The experiments has been performed by changing the catalyst dosing rate in the range of 20 to 100 mg. the experiments has been performed for 50 minutes to optimise catalyst dosing, rpm of magnetic stirrer, pH of solution and cadmium concentration of the solution. The removal of cadmium from the polluted water is studied in 10 minutes interval upto 70minutes.

b. Preparation of bio-adsorbent:

Seeds of jackfruit (JFS) has been taken and washed with tap water to remove sand particles and other impurities on it. After washing, seeds are kept in oven for 48 h with maintaining 60^{o}C for drying purpose. The Fig. 1 shows the dried seeds which is ready for crushing and milling to make it powder form. The powder has been kept in sheave shaker and all equal size particles have been distinguished. The higher size particles have been again crushed to find minimum particle size. After getting all equal size particles the powder sample has been send for different types of characterisation and again calcined it at 400^{o}C for 3hrs.

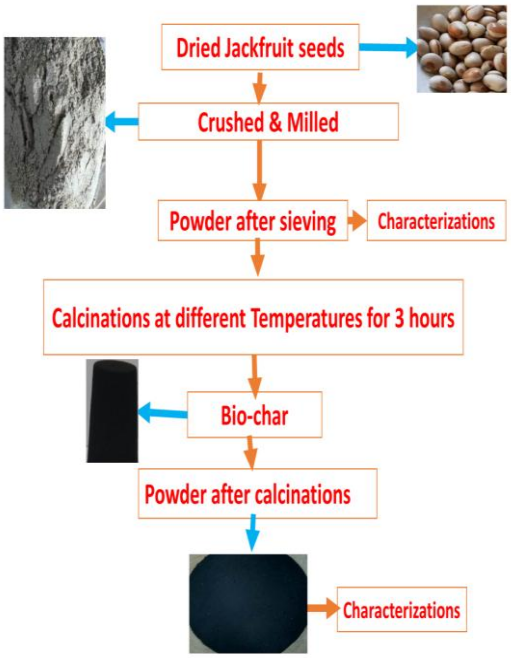

Fig. 1. Flow chart of jackfruit seeds based bio-adsorbent

c. Catalyst Characterization

Thermo gravimetric analysis (TGA) and Differential Thermal Analysis (DTA) performed on a Shimadzu (Japan; DTG-60) in Nitrogen environment, at a different heating rate of 10-50ºC/min. FTIR spectrum of the prepared catalyst was recorded in the range of 400-4000 cm^{-1} using Shimadzu (Corporation, Japan; IR-Prestige 21). The elemental analysis by Inductively Coupled Plasma Optical Emissions spectrometer in Perkin Elmer, Optical 2100DV ICP-OES (USA) with Spectral Range of 160-900nm, spectral Resolution of 0.009 nm at 200nm and speed of 20-25 elements in less than 5 min.

d. Experimental Design:

All the experiments have been designed with the help of Design-Expert 6.0.8. Response surface methodology has been used to optimize the process parameters for maximizing the % pollutant removal from waste water. Within this methodology, a four factor and five level central composite design (CCD) has been implemented to study the combined effect of all the four parameters (Pollutant concentration (A), mixing speed (B), pH (C) and Catalyst dose (D)) on the percentage removal of pollutant from wastewater (Park et al., 2010). The range and levels of all the four selected parameters studied in the experiments have been presented in Table. 2.1.

Variables	Range and level	
	Low	High
Pollutant concentration (A), ppm	0.5	2.5
mixing speed (B), rpm	110	150
pH (C)	3	11
Catalyst dose (D), mg	20	100

2.5 Thermal Kinetic Theoretical Approach:

The common rate equation governs in all kinetic studies can be generally written as follows:

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \quad (1)$$

Where is the rate of conversion at a constant temperature, $f(\alpha)$ is the reaction model which describes the changes in the physical or chemical properties, k is the rate constant, dependent on temperature T.

The conversion rate α (using TGA records) is defined as:

$$\alpha = \frac{w_o - w_t}{w_o - w_f} \quad (2)$$

Where , and are the initial mass of the sample at t=0, mass of the sample at time t and mass of the sample at final degradation respectively.

According to the Arrhenius relationship, the rate constant is the function of temperature and can be written as follows:

$$k(T) = k_0 \exp\left(\frac{-E}{RT}\right) \quad (3)$$

wherek_0 is the pre-exponential factor, *R* is the gas constant (8.314 J/K mol), *and E*is the activation energy (kJ/mol).

Using equation (1) and (3) following equation can be derived:

$$\frac{d\alpha}{dt} = k_0 \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (4)$$

Equation (4) describes the relationship between the conversion rate, rate constant and temperature which is used for recording the experimental data. To conduct kinetic study in TGA one of the ways is to use a heating rate, $= {}^{dT}/_{dt}$. Eq.(4) can be written as follows:

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (5)$$

Equation (5) is most basic equations used for kinetic study of thermal degradation.

E, activation energy can be estimated using various models. Generally used methods are Kissinger, Friedman, Flynn and Wall, Coats-Redfern, and Flynn-Wall-Ozawa (F-W-O) (Flynn and Wall, 1966; Mishra and Mohanty, 2018; Gogoi et al., 2018**).** In this study, we used F-W-O method which gives slope (-E/RT) from the line obtainedby plotting log β against 1/T at fixed degree of conversion.

F-W-O fitting equation is given below (Oza et al., 2014):

$$\log f(\propto) = log\left\{\frac{k_0 E}{R}\right\} - \log\beta - 2.315 - 0.4567\ \frac{E}{RT} \quad (6)$$

III. RESULT AND DISCUSSION

a. FTIR analysis

The FTIR spectral analysis revealed several functional groups on the surface of biomass shown in Fig. 2. The absorption peak observed at wave-number 3279 cm^{-1} is associated with O-H stretching vibration. The wave-numbers around 2927 cm^{-1} and 2364 cm^{-1} are corresponding to the C-H aliphatic stretching vibration. The peak displayed at 1643 cm^{-1} is attributing to the stretching band of the carboxyl double bond from carboxyl functional group. The peak around 1150 cm-1 is indicative of P=O stretching present in phosphate group. It has been observed by the (Kim et al., 2015). Kim et al., 2015 the carboxyl groups present in biomass plays a significant role in the cation metal removal. The peak displayed at wavenumber 1007 cm^{-1} is assigned to the O-H stretching of primary alcohol group. The peak at 929 cm^{-1} shows the C-C links in the biocarbon. The presence of polar groups on the biocarbon surface is likely to provide the considerable cation exchange capacity to the absorbent (Ghani et al., 2009).

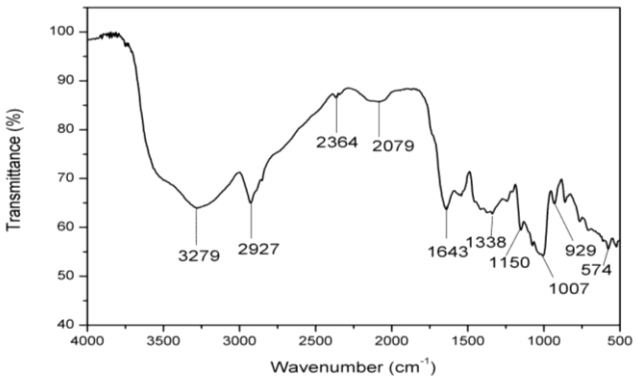

Fig. 2. FTIR spectra of jackfruit seeds

b. Thermo-gravimetric Analysis

The curve of TGA and DTAwere used to study the thermal degradation behaviour of JFSP, as shown in Fig. 3. The DTA plot of JFSP shows three major endothermic peaks which indicated decomposition occurs in three main processes. The initial weight loss of~10% in the temperature range of 30-150^oC, mainlycorresponds to the evaporation of physically absorbed water. DTA curve also shows first sharp endothermic peak at 59^oC with change in enthalpy of -1.4 kJ/g. TG curve revealed that above 150^oC, thermal stability is gradually decreasing and decomposition of the JFSP occurs with the complete decomposition at 626^oC. The second stage decomposition process occurs in the temperature range of 150-332^oC (weight loss~ 64%), showing second endothermic peak at 152^oC with change in enthalpy of -1.67kJ/g. This result is attributed to the thermal depolymerisation of hemicelluloses, pectins, the cleavage of glycosidic linkage of cellulose and some parts of lignin (Theivasanthi et al., 2011; Arbelaiz et al., 2006; Monteiro et al., 2012). At a temperature range of 350-625^oC, third and last stage decomposition process occur at peak 415^oC (change in enthalpy of -3.02 kJ/g) showing weight loss of~ 99%. This indicates the thermal degradation reactions taking place for the major constituent of the biomass that is cellulose and remaining lignin (Benitez et al., 2014; Prasad et al., 2014).

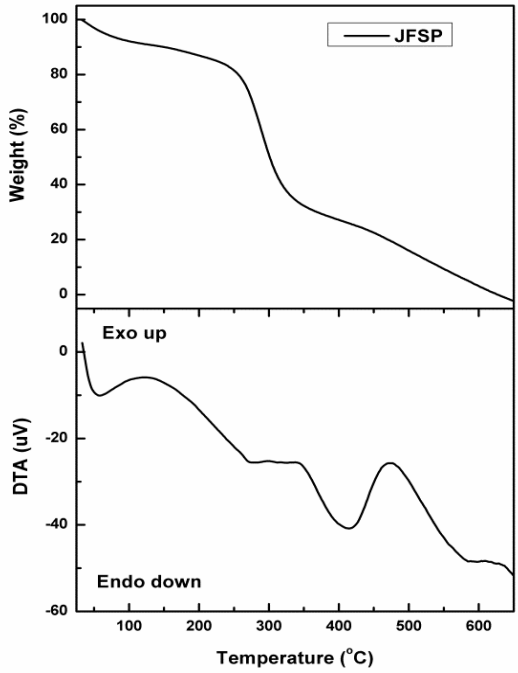

Fig.3. TG-DTA thermograms of jackfruit seeds

c. Thermal Kinetic Study

Activation energy was estimated using TGA data at five different heating rates (10-30^oC/min). The average activation energy was determined using isothermal F-W-O method from the thermal degradation conversion range of 0.1-0.9**. Fig.4** shows the linear plot JFSP at various conversion rates. At various thermal degradation conversion rates, Activation energy was estimated from the slope of the curves. Summary of the activation energy values with R^2 values are given in **Table 2**. From the result, it can be observed that the activation energy varies with the varying rate of conversion, indicating high degree of probability to present more than one step reaction. Higher activation values are observed in the middle con version rate (0.3-0.6) whereas lower activation energy values were observed for lower and higher conversion rate. Activation energy is the minimum amount of energy required to initiate a reaction. Activation energy is

dependent on the pyrolysis reaction mechanism; higher value of activation energy indicates slower reaction **(**Mishra and Mohanty, 2018**).** This variation in activation energy is probably observed due to the mechanism involving the thermal decomposition of the biomass matter is different. This could be explained by the TGA curve (**Fig. 4).** The thermal degradation temperature forα = 0.1-0.2 is around 270^{o}C and for α = 0.5 is around 312^{o}C. This is the part of the TGA curve where maximum thermal degradation takes place. The observed activation energy is 130.69 kJ/mol, which corresponds to the degradation of hemi-cellulose, cellulose and lignin (Oza et al., 2014). According to Mohamed, 2013,value of the activation energy indicates about the type of adsorption taking place, which is physical or chemical adsorption. For the physical adsorption processes activation values usually found in the range of 0-40 kJ/mol, while higher activation energies values i.e in the range of 40-800 kJ/mol indicates chemical adsorption processes.

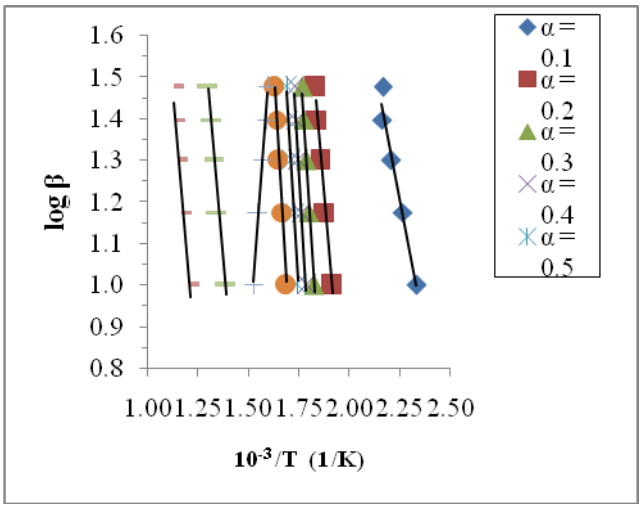

Fig. 4 Curves of fitting to kinetic model proposed by Flynn-Wall-Ozawa (F-W-O) to various conversion percentages

Table 2. Kinetic parameters obtained from F-W-O method with fitted equation for Jackfruit (JF) power

Conversion rate (α)	Equations	R^2	E, (kJ/mole)
0.1	y = -2.5565x + 6.9645	0.97	46.54
0.2	y = -5.4866x + 11.498	0.98	99.88
0.3	y = -8.0076x + 15.621	0.99	145.77
0.4	y = -8.3145x + 15.835	0.99	151.36
0.5	y = -8.5099x + 15.862	0.99	154.92
0.6	y = -7.8898x + 14.329	0.99	143.63
0.7	y = 6.5171x - 8.9333	0.99	120.02
0.8	y = -5.4511x + 8.5543	0.97	99.23
0.9	y = -5.8823x + 8.1026	0.97	107.08

d. Statistical Analysis

The results are obtained in terms of percentage removal of cadmium from the polluted water for all the individual experiments and then statistical analysis has been performed by using the Design-Expert. The optimisation study has been conducted with Design-Expert software to maximize the percentage removal and is presented in the following subsections. According to the design discussed in the earlier section, a total number of 30 experiments have been conducted. For the further study these values have been fed to the Design-Expert software, which helps to predict the model (quadratic equation). This equation relates the independent variables (*A, B, C and D*) and dependent variable (% removal) as shown in eq. (7).

$$Y = ++33.61+13.22A+0.39B+3.67C+0.322D-2.54A^2-0.0001B^2-0.158C^2-1.27D^2$$
$$-0.062A*B+0.187A*C+0.0187A*D-0.015B*C-0.0015B*D+4.68C*D$$

where *Y* is the cooling rate and A, B, C and D are Pollutant concentration, mixing speed, pH and bio-adsorbent dose respectively. The value of correlation coefficient R^2, used to check the model validity, is found to be 0.92.

e. Effects of pH

The effect of pH was studied from a range of 3-11 under the precise conditions at an optimum contact time of 1 h with 25 mg of the adsorbents used for 100 mL of contaminated water, and at a room temperature and it was observed that with increase in the pH (3-8) of the wastewater, the percentage removal of cadmium ion increased up to the pH 7-8 as shown in **Fig.5**. At pH 7.5, maximum removal was obtained for metal ions, with 96.7%. The increase in percentage removal of the metal ions may be explained by the fact that at higher pH the functional groups in the adsorbent surface were deprotonated and become negatively charged and while at lower pH, adsorption rate decreases and this is because at lower pHs, there is competition between H+ ions and cadmium ions (Mohamed, 2013).

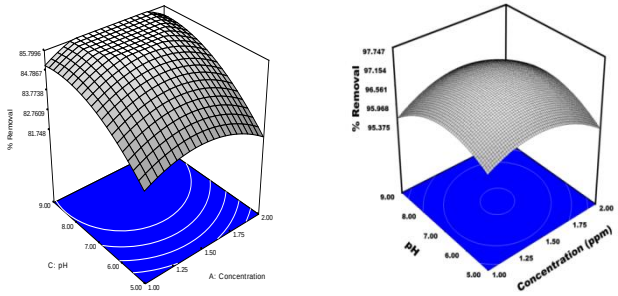

Fig.5. Effects of pH on cadmium removal

f. Effects of Concentration and Steering Speed

The effect of initial concentration 0.5 to 2.5 ppm was investigated at ambient temperature with regular intervals of 10 to 70 min for the adsorbent dosage of 20-100mg and steering speed ranges 110-150 rounds per minutes. From the obtained result (**Fig. 6**), no significant change has been observed for the percentage removal of metal ions with the increase in initial concentration of cadmium ions. This is probably because of the removal of cadmium ions by forming complex with bio-adsorbent (Mohammad et al., 2018).This observation indicates that the adsorption of cadmium by JFSP is mostly depends upon the number of active sites present which can be able make complex with the metal ion. Similar result has also been reported by Mohammad et al. 2018, which shows saturation point at the same time interval for different initial conc. This corresponds to the availability of more vacant biding sites for cadmium adsorption during initial contact times (Pandey and Tiwari, 2015).

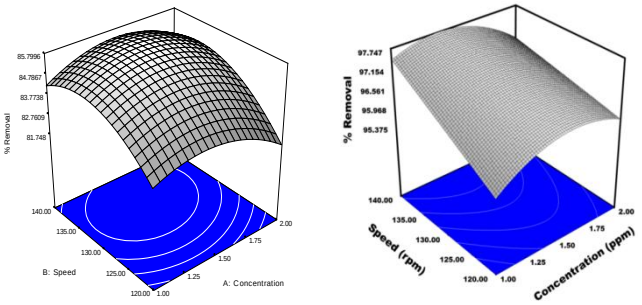

Fig. 6. Effects of Concentration and Steering Speed on cadmium removal

g. Effects of Catalysts Dosing:

For the present study, effect of variation in dosing (25-100 mg) was analyzed under the specified conditions at amibent condition. Sample was collected for the analysis of percentage removal of cadimium in the regular interval of 10 min for the period 1 h. From the experimetal results shown in Fig.7, it can be clearly seen that the percentage removal of metal ions has been increased with the increase in adsorbent dosing. Maximum adsorption efficiency of about 97.12% was observed even at lower adsobent dosing of 60 mg for 100 mL cadimium ion. Futher increase in adsorbent dosing has not been shown any significant effect on the sorption. This is probabily because of the availability of more binding binding sites at higher dose of bio adsorbents (Devi et al., 2017).

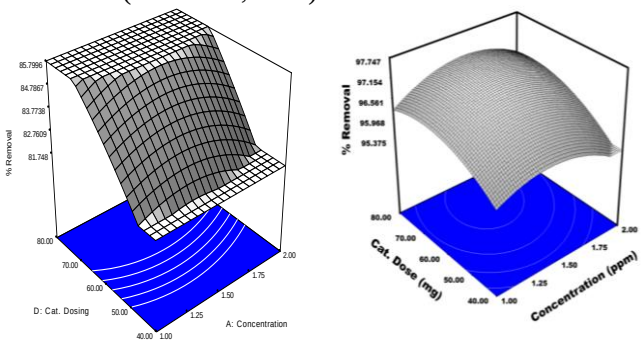

Fig. 7. Effects of dosing of adsorbent on cadmium removal

IV. CONCLUSION

JFSP was used as a bio-adsorbent for the removal of Cadmium from the synthetic wastewater. FTIR analysis shows the presence of carboxyl group in JFSP biomass which plays a significant role in the metal removal and the presence of polar groups on the bio-absorbent surface is likely to provide the considerable cation exchange capacity to the absorbent. TGA analysis shows maximum thermal decomposition in the range of 150-380^{o}C. Activation energy was observed 130.69 kJ/mole using F-W-O method which attributed to a chemisorptions adsorption process. JFSP based bio-adsorbent was used successfully to remove cadmium ions from synthetic wastewater ~97% in one hour at 120 rpm speed and pH 7-8. This study shows a new trend for using waste materials as an adsorbent for the benefit of pollution control.

V. ACKNOWLEDGEMENTS

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