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EXTRACTION AND APPLICATION OF CELLULOSE FROM RICE HUSK IN ADSORPTION OF FLUORIDE FROM CONTAMINATED WASTE WATER

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ABSTRACT

Rice Husk (RH) has 32.24% cellulose content; and the annual rice husk produce in India amounts to approximately 120 million tons. Cellulose was extracted from raw RH using alkaline hydrolysis, followed by bleaching treatment and acid hydrolysis and critical point drying. The synthesized cellulose was characterized by Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET). The adsorption capacity of cellulose in fluoride solution was measured by electrode type fluoride meter. Adsorption studies were carried out by varying several parameters like adsorbent dosage(g/L), initial concentration(mg/L), pH, contact time(min), temperature(°C) and agitation speed(rpm). The adsorption efficiency of the obtained cellulose was measured in terms of removal percentage(%) and adsorption capacity(mg/g). The adsorption kinetics, isotherms and thermodynamics were investigated in detail to gain insights into the adsorption process. The experimental data from batch study was evaluated using Langmuir and Freundlich adsorption isotherm models to evaluate distribution of active sites on adsorbent surface and adsorption capacity(mg/g). The results show that the BET surface area of the cellulose reached $76.15 m^2/g$. The Langmuir capacity of the cellulose in fluoride adsorption was 5.102mg/g at 300 K and pH 7. Cellulose extracted from RH appears to have profitable and parsimonious features to be termed as eco-friendly adsorbent.

Key Words : Rice Husk, Critical point drying, Cellulose, Fluoride, Adsorption, Isotherm model, Kinetic model.

INTRODUCTION

The UN had estimated that the amount of wastewater produced annually is about 1500 km^3, six times more water than exists in all the rivers of the world in 2003, on the other hand Vié, Hilton-Taylor, & Stuart in 2009 studied that in some regions of the world, more than 50% of native freshwater fish species were at risk of extinction, and this is also the case for nearly one-third of the world's amphibians. Both of these observations emerged into bitter truth of mother nature.[1-3] The city of Cape town became the 1st city to run out of their fresh water reserve in 2018. A pond near Wuhan, China; they say 275,000 pounds of fish died in three days due to water pollution in 2014.[4]

Seawater fluoride levels are usually in the range of 0.86 to 1.4 mg/L, and average 1.1 mg/L or ppm[1]; whereas surface water such as rivers or lakes generally contains between 0.01–0.3 ppm. The natural levels of under 0.05 mg/L have been detected in parts of Canada but up to 8mg/L in parts of China; in general levels rarely exceed 10 mg/litre. The maximum safe daily consumption of fluoride is 10 mg/day for an adult according to U.S. or 7 mg/day according to European Union. [5-7]

Fluorosis is most severe and widespread in the two largest countries that is India and China In India, 20 states have been identified as endemic areas, with an estimated 60 million people at risk and 6 million people disabled; about 600,000 might develop a neurological disorder as a consequence[2]. In India, the most common cause of fluorosis is fluoride-laden

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drinking water which is sourced as groundwater from deep-bore wells. Over half of groundwater sources in India have fluoride above recommended levels[3,8-11]. UNICEF estimates that "fluorosis is endemic in at least 25 countries across the globe.

At higher concentrations of Fluoride; it has certain health hazards such as; thyroid and neurological problems, In some cases, excess fluoride can also damage the parathyroid gland. This can result in hyperparathyroidism, which involves uncontrolled secretion of parathyroid hormones. Which can further result in a depletion of calcium in bone structures and higher-than-normal concentrations of calcium in the blood[4,12-13].

In 2014, fluoride was documented as a neurotoxin that could be hazardous to child development, along with 10 other industrial chemicals, including lead, arsenic, toluene, and methyl-mercury (FDA).

Moreover high concentration of Fluoride may also cause acne and other skin problems, cardiovascular problems, including arteriosclerosis and arterial calcification, high blood pressure, myocardial damage, cardiac insufficiency, heart failure. Also problems like reproductive issues, such as lower fertility and early puberty in girls, thyroid dysfunction conditions affecting the joints and bones, such as osteoarthritis, bone cancer, and temporo mandibular joint disorder (TMJ), neurological problems leading to Attention deficit hyperactivity disorder (ADHD).

Fluoride enters human body by ingestion and inhalation. While ingested; it reacts with HCl in stomach and converts into HF, then through Gastrointestinal track it reaches tissues and bones. At molecular level it reacts with calcium present in bones. The reaction of Ca^{2+} ions in bones and HF forms an insoluble salt, CaF. This process results in incr eased density, but decreased strength in bones.

Non-dental sources of fluoride include: drugs containing perfluorinated compounds food and beverages made with water that contains fluoride, pesticides, waterproof and stain-resistant items with PFCs,

Some geographical areas have drinking water that is naturally high in fluoride, for example, southern Asia, the eastern Mediterranean, and Africa.

Fluoride concentration in groundwater can range From greater than 1 mg/L to lesser than 35 mg/L[5]. The acceptable Fluoride concentration range in drinking water is 0.5–1.5 mg/L. Approximately, 260 million people worldwide (in 30 countries) are drinking water with F- greater than 1.5 mg/L[6]. In India, groundwater F contamination is a major problem in 17 states (of 29) and endemic fluorosis is found to affect about one million people especially in Andhra Pradesh, Assam, Gujarat, Rajasthan, Tamil Nadu, and Uttar Pradesh[7, 15].

Cellulose nanomaterials (CNs) can be isolated from various natural resources like plant, animal, or mineral plants. Two general type of cellulose nanomaterials (CNs) arecommonly known as cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). CNCs particles are highly crystalline in nature (at least one dimension should be equal or less than 100 nm) [8]. It can be used as a cheaper adsorbent for removing s from aqueous solution directly[9,10]. Nanocellulose having high surface area, high mechanical strength, chemical inertness and hydrophilic surface makes it a very efficient material in membranes and filters, for adsorbing impurities from industrial effluents and drinking waters. These have high mechanical strength and rigidity[1,6].

RHA is widely used for   removal. It contains 32.24% cellulose. Thus Rice husk was chosen because of their granular structure, chemical stability and its local availability at very low cost.

In this study cellulose was extracted from washed raw rice husk and tested for its adsorption capacity by batch adsorption study.[16-18]

MATERIAL AND METHODS

Raw rice husk

Was collected from farmers of Medinipore district and was washed several times with water followed by filtration. The cleaned rice husk was oven dried completely at 120° C, cooled and then sieved. 80-100 μm particle

size was used without further treatment. The adsorbent was stored in desiccators for further use.[19,20]

Isolation of cellulose

For 10g of raw rice husk 100ml of 0.75% sodium chlorite (Merck Life Science private limited) solution was used to bleach and was kept for 1 hour at 45°C with continuous stirring. The treated mass was filtered, washed with distilled water until it reached to pH 5 and put into 2% sodium hydrogen sulfite (Merck Life Science private limited) solution for 30 minute. It was then filtered, washed with distilled water. The dried mass was then treated with 17 % NaOH(Merck Life Science private limited.) solution at 80°C for 15min to remove hemicelluloses and SiO_2. Finally this chemically treated mass was filtered, washed with distilled water to remove the alkali until to neutral pH.[21-24]

Nanocellulose preparation

Hemi cellulose and lignin free cellulose was acid hydrolyzed for 3 hours at 50oC with constant stirring. For 1g of cellulose 20 ml of 20% H_2SO_4 (w/w) solution (Merck Life Science private limited) was used. After that excess acid was washed with distilled water to pH about neutral. Hydrolysis process was followed by centrifugation and freeze drying. [25]

Fluoride solution preparation

In this study, Sodium fluoride (Loba. Chemie) stock solution of 1000 ppm concentration was prepared and solutions of different concentrations ranging from 1-50 Fluoride/L were made by further dilutions.[26,27] The absorbance of solution was measured using electrode type fluoride meter (Thermo Scientific Orion Star A214).

Analysis

FT-IR spectroscopy of the samples as powder-pressed KBr pellets were examined in the wave number range from 4000 to 450 cm^{-1} at a resolution of 4 cm^{-1} using Spectrum Two(Perkin Elmer) spectrophotometer at room temperature. The structure and the composition of products were analyzed by X-ray powder diffraction (XRD) (SHIMADZU XRD-6000 diffractometer employing Ni-filtered Cu Ka radiation, at a scanning rate of 6o/min with 2 theta ranging from 5o to 60°). SEM (Carl Zeiss MinSCAN) analysis of the prepared adsorbent was done at 2, 5 10 KX.[28,29]

Batch adsorption study

Was carried out in 100 mL conical flask containing 50 mL of a fluoride solution in a rotary shaker (GB Enterprises) by varying several process parameters like adsorbent dosage (g/L), initial concentration (Fluoride/L), pH, contact time(min), temperature (°C) and agitation speed(rpm); followed by centrifugation. Concentration of Fluoride was determined by electrode type fluoride meter(Thermo Scientific Orion Star A214).

The pH of the solution was adjusted using 0.1 M NaOH(Merck Life Science private limited) and 0.1 M HCl(Merck Life Science private limited) solution. The Isotherm study was done by varying the concentration of solution (1ppm to 50ppm) keeping temperature constant and agitated at 120 rpm. The kinetic study was carried out with different contact time (15min to 180min). Thermodynamic study was done with varying temperature (25 °C to 40 °C).

RESULTS AND DISCUSSION

Effect of pH

As shown in **Fig. 1**, pH plays an important role for fluoride removal on RH cellulose. Initially the pH of the solutions was adjusted pH range from 2-10 by adding HCl and NaOH solution. With increasing pH value from 2 to 10 adsorption capacity decreases from 9.4mg/g to 3.109mg/g. Fluoride is favorably adsorbed on positively charged surfaces. Protonation increases in strong acidic solutions. Due to presence of excess H^+ ion in lower pH solution and having small ionic radius H^+ can be adsorbed easily onto cellulose surface. Anionic fluoride can be adsorbed better onto the positively charged cellulose. With increasing pH, more negatively charged adsorption sites will be available reducing adsorption capacity. At higher pH better removal is observed as fluoride precipitates at basic environment. At lower pH electrostatic attraction between cellulose surface and anionic fluoride becomes

stronger[11]. However water treatment at such acidic environment is impractical thus we performed all study at pH 7.

Effect of contact time

Variation in contact time plays important role in determining the efficiency of the adsorption. As **Fig. 2**, Batch equilibrium studies were carried out at 35°C by adding 0.1 g (2g/L) of adsorbent to 10mg/L Fluoride solution of 50 ml volume at neutral pH .The flasks were agitated in B.O.D shaker at 120 rpm for equilibrium time. Samples were taken at different time interval (15, 30, 45, 60,120,180 min) and concentration was analyzed by electrode type fluoride meter (Thermo Scientific Orion Star A214).

The adsorption capacity increases till the contact time increases up to 2 h and then it attained saturation. It was observed that increasing agitation time from 15 min to 120 min removal efficiency of Fluoride on Cellulose increases from 2.091mg/g to 5.310mg/g.

Effect of adsorbent mass

The removal efficiency was increased as the adsorbent masses were increased from 2g/L to 10g/L for 50 ml of Fluoride solution at equilibrium time. As shown in **Fig. 3**, It was observed that removal of Fluoride changes from 4.901mg/g to 5.710mg/g with increasing adsorbent mass. From **Fig. 3** it is readily estimated that by increasing the amount of adsorbent, the number of active adsorption sites and the surface area increases, therefore, removal efficiency increases. So in this work adsorbent dose of 2g /L was kept constant for further investigations.

Effect of initial concentration

Fig. 4, shows the effect of initial concentration on the Fluoride removal efficiency by cellulose.

The effect of Fluoride concentration (2 to 10 mg/L) was studied by adding adsorbate of 0.1g (2g/L) at mixing rate 120 rpm. It has been observed that the adsorption efficiency gradually decreases with increase in concentration until the equilibrium is reached. The Fluoride removal efficiency on Cellulose decreased from 7.98mg/g to 5.173mg/g. The equilibrium conditions were reached within 2 hours.

Effect of temperature

Removal efficiency increases with increase in system temperature. In our work it was found that the removal efficiency decreased from 4.981mg/g to 2.101mg/g with the increasing temperature from 25 °C to 45°C. In **Fig. 5**, was observed that maximum Fluoride adsorption was 4.981mg/g at 35 °C. It is well known that the mobility of molecules may be enhanced by increasing the system temperature that lead to reduce in active sites on adsorbent surface. At higher temperature violent molecular motion facilitates desorption process[12] which reduces the adsorption capacity.

Adsorption isotherm

Fig. 6, shows Freundlich model for Fluoride adsorption by Cellulose. Calculated parameters for Langmuir isotherms and Freundlich isotherm models are shown in **Table 1** and **Table 2**. The adsorption of Fluoride on cellulose fitted Freundlich model very well with the correlation coefficient R^2= 0.9906, i.e, better than Langmuir Isotherm with R^2=0.9510. Fluoride adsorption process using Cellulose was fitted better by Freundlich isotherm because of heterogeneous surface active site distribution on adsorbent[13]. A value of 1.7999 obtained for Freundlich constant (n) indicates the condition of favorable adsorption process[8]

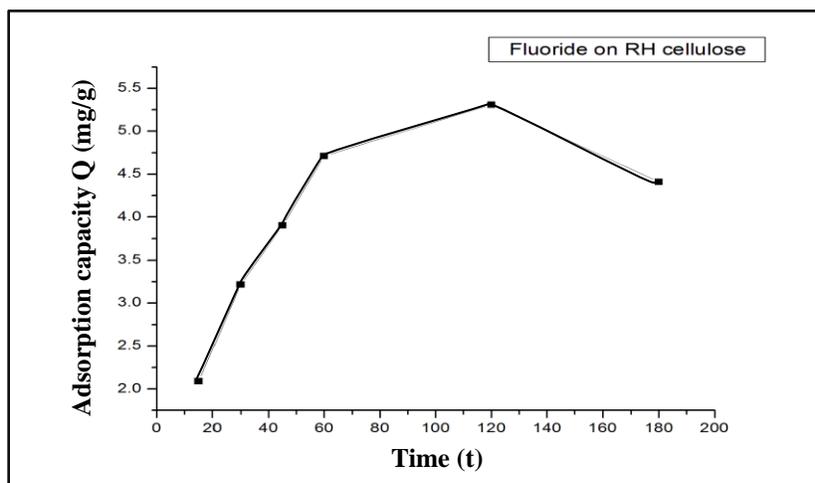**Table 1 : Calculated parameters of Langmuir Isotherm**

Adsorbent	Temp(^{o}C)	k (L/gram)	Qo(mg/gram)	R^2
RH cellulose	30	0.08047	5.102	0.9510

Table 2 : Calculated parameters of Freundlich Isotherm

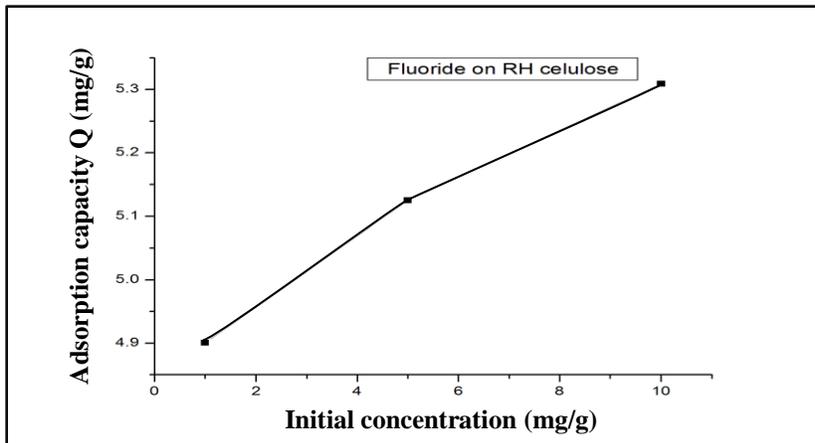| Adsorbent	Temp(^{o}C)	K_F (L/mg)	n	R^2
RH cellulose	30	0.6192	1.7999	0.9906
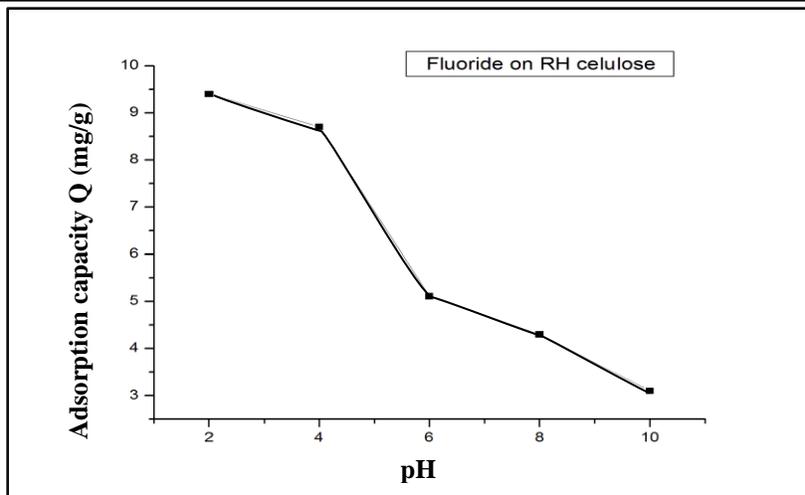
Fig. 1 : Effect of pH on % removal

Fig. 2 : Effect of time on % removal
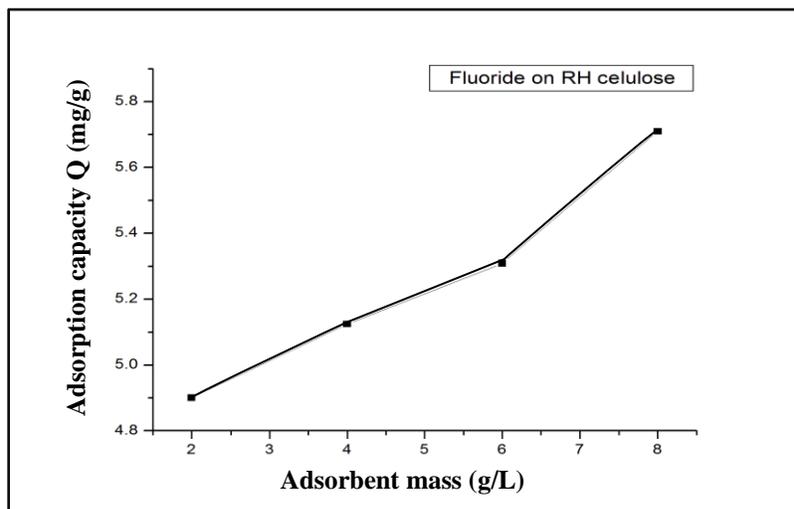
Fig. 3 : Effect of adsorbent mass on % removal

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Fig. 4 : Effect of initial concentration on % Removal
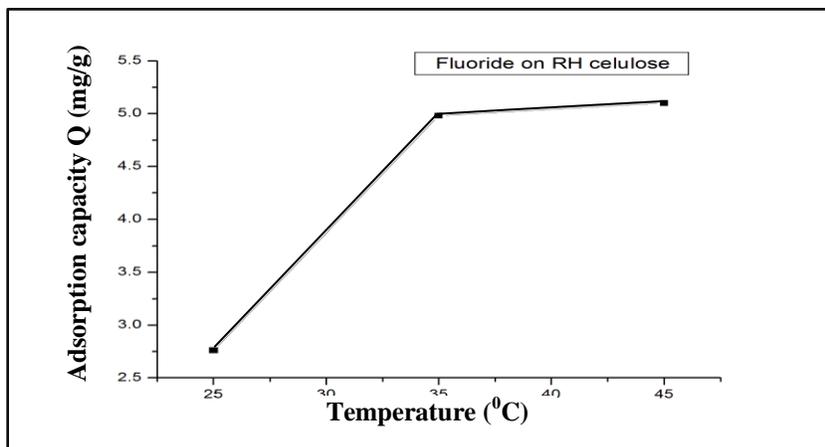
Fig. 5 : Effect of temperature on % Removal
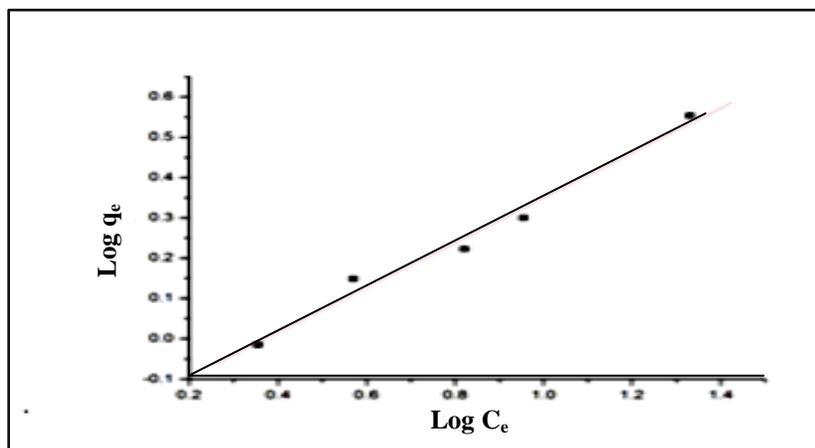
Fig. 6 : Freundlich isotherm

CONCLUSION

The study revealed that the BET surface area of the cellulose reached $76.15 m^2/g$ and adsorption of Fluoride on cellulose extracted from rice husk was maximum at pH 7.0 with 2g/L of adsorbent at 35 ^{o}C within equilibrium period of 2 hours. The maximum adsorption efficiency was 76.55% with an adsorption capacity of 5.102 mg/g. the adsorption

isotherm study showed that the distribution of active sites on adsorbent was heterogeneous in nature.

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