

REMOVAL OF Fe(III) FROM AQUEOUS SOLUTIONS USING RICINUS COMMUNIS SEED SHELL AND POLYPYRROLE COATED RICINUS COMMUNIS SEED SHELL ACTIVATED CARBONS

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ABSTRACT: The objective of this study is to assess the removal of Fe(III) from aqueous solutions onto activated carbons prepared from Ricinus Communis Seed Shell. The effects of various parameters have been investigated by the following batch adsorption technique. The various variables studied include initial concentration of the adsorbate, agitation time, adsorbent dosage, pH, kinetics, influence of co-ions and temperature. The experimental data was fit well to the Freundlich isotherm. Thermodynamic parameters such as ΔH° , ΔS° , and ΔG° were calculated, indicating that the adsorption was spontaneous and endothermic nature. FT-IR and SEM patterns of the before and after adsorbent were recorded to get better sight into the mechanism of adsorption process.

KEYWORDS: Adsorption, Fe(III), Ricinus Communis, Activated carbon, Poly pyrrole and Adsorption Isotherm.

1. INTRODUCTION

The organic pollutants, which can be bio-degraded, heavy metals don't degrade into harmless end product [1]. Iron is one of the major constituents of the lithosphere and comprises approximately 5% of it. It is routinely detected in municipal waste effluent, particularly in cities where iron and steel are manufactured. Iron readily complexes with sulphates in the sediments of many surface levels of water. The primary concern about the presence of iron in drinking water is its objectionable taste. The taste of iron in drinking water can be easily detected even at low concentrations of about 1.8 mg/L [2]. There are many problems that result from iron toxicity. These include anorexia, oliguria, diarrhoea, hypothermia, diphasic shock, metabolic acidosis and even death. In addition to these, the patient may experience vascular congestion of the gastrointestinal tract, liver, kidneys, heart brain, adrenals and thymus. With acute iron poisoning, much of the damage happen to the gastrointestinal tract and liver which may result from

the high localized iron concentration and free radical production leading to hepta toxicity via lipid peroxidation and destruction of the hepatic mitochondria. As a result of iron storage disease, the liver becomes cirrhotic. Hepatoma, a primary cancer of the liver, has become the most common cause for death among patients with hemochromatosis [3]. This is an iron storage disease that results from the inability of the intestine to keep out unwanted iron. Instead, this iron accumulates in the liver causing siderosis and causes damage to the storage organs. Also, when siderosis becomes severe in young people, it leads to myocardial disease which is a common cause of death. Impotence may also occur in young men and amenorrhoea in young women. Both these problems relating to reproduction are due to iron loading in the anterior pituitary [4].

Different cheap adsorbents like peat, marine algae, clays, maize cob, bagasse, palm fruit bunch, saraca indica leaf are used[5]. The present study undertaken to removal of ferric ion from aqueous

solutions using Ricinus Communis seed shell(RCC) and Polypyrrole coated Ricinus Communis seed shell activated carbons(PPy/RCC) as an adsorbent. It is a polysaccharide, non-toxic, economically favorable one [6]. It is insoluble in water and alkali but soluble in strong mineral acids. It forms complexes with transition metal ions. Systematic studies of the adsorption of ferric ion by RCC and PPy/RCC under different experimental conditions have been carried out to understand the nature of the adsorption process.

2. EXPERIMENTAL METHODS

Activated carbons were prepared from Ricinus Communis seed shell (RCC) and PolyPyrrrole coated Ricinus Communis seed shell activated carbons (PPy/RCC). The raw material (Ricinus Communis seed shell) was procured from local vendor. The material was washed in hot distilled water to remove earthy matter, cut into small pieces and dried. The activated carbon was prepared from the above material impregnated with concentrated sulphuric acid. For impregnation, a ratio of acid volume to weight of precursor of 1: 1 was employed. After that, the charred material was washed several times in distilled water until the pH of the washings becomes neutral. Then the material was dried and carbonized at 500°C using muffle furnace. Finally, the activated was ground and sieved to 180 μ using standard sieves. All the reagents used for this study are commercially available Analar grade (Merck, SRL, India and SD-fine, India).

A stock solution of the adsorbate containing 1000 mg/L of Fe(III) was prepared by dissolving the calculated quantity of Ammonium Iron(III) sulphate dodecahydrate in doubly distilled water. Double distilled water was used through out the experiments. The adsorption experiments were carried out by batch equilibrium method. 50 ml of the adsorbate solution was agitated with 50 mg of the prepared adsorbent in a temperature controller water bath shaker (Techno Make). The samples were with drawn after specified time interval and centrifuged, the supernatant solution was analysed for the residual Fe(III) concentration using Spectrophotometer (Make: Systronics 169) at an absorption wavelength of 480 nm. For the effect of temperature, the experiments were carried out at temperatures of 303, 313 and 323 K.

Pyrrrole used as a monomer for preparing PPy/RCC. In order to prepare PPy/RCC, 5.0g RCC (180 μ) was immersed in 50 ml of 0.2M freshly prepared pyrrole solution for 12 hours before polymerization. The excess of the monomer solution was removed by simple decantation. 50ml of 0.5M ferric chloride –oxidant solution was added into the mixture gradually and then the reaction was allowed to continue for another 2 hours at room temperature.

The coated RCC polymer filtered, washed in distilled water, then dried at 60°C in a hot air oven and sieved for further use [7].

3. RESULTS AND DISCUSSION

3.1. Adsorbent Characterization

All the parameters were analyzed using standard testing methods [8]. Activated carbons are widely used adsorbent due to its high adsorption capacity, high surface area, micro porous structure and high degree of surface respectively. The chemical nature and pore structure usually determine the sorption activity. Some important physico-chemical Characteristics of RCC are presented in table 1.

3.2. Effect of adsorbent dosage, pH and Agitation time

These experiments are done by using 50mg to 250mg of adsorbents, 50ml of 50ppm of Fe(III) solution and agitation of various time intervals[9,10]. The results indicate that the optimum dose is fixed as 50mg due the quantity of Fe(III) uptake more, the optimum pH is fixed as 4 due to maximum removal of Fe(III) and the optimum agitation time is fixed as 30 minutes due to after this time removal of Fe(III) is constant[11,12].

3.3 Adsorption Isotherms

The Langmuir isotherm can be expressed as;

$$q_e = \frac{Q_0 \cdot b_L \cdot C_e}{(1 + b_L \cdot C_e)}$$

Linear form of the rearranged Langmuir mode[13] is

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b_L} + \frac{C_e}{Q_0}$$

The constants Q_0 and b_L can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e .

The Freundlich equation is expressed as;

$$q_e = k_f C_e^{1/n}$$

Linear form of Freundlich equation[14] is

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

When $1/n$ is >1.0 , the change in adsorbed metal ion concentration is greater than the change in the solute concentration.

The essential characteristics of the Langmuir equation can be described by dimensionless equilibrium parameter R_L which is defined by Hall et al as,

$$R_L = 1 / (1 + b_L \cdot C_0)$$

Where, b_L = Langmuir constant, C_0 = Initial concentration of Fe(III) (mg/L)

The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Based on R_L values which is favorable one.

The adsorption data have been fitted to the Freundlich isotherm which have high correlation coefficient value ($r^2=0.9981$) in table 2. The linear plots of $\log q_e$ versus $\log C_e$ at different temperatures are shown in figure 1. The results indicate that Freundlich adsorption isotherm model fits very well for the selected adsorbent - adsorbate system. The results indicate that the adsorption capacity of the adsorbent increases with increase in temperature. The value of intensity of adsorption (n) is greater than unity signifies that the forces within the surface layer are attractive [15].

3.4 Thermodynamics Parameters

The standard free energy change, enthalpy and entropy changes along with equilibrium constants were computed [16] and are given in table 3. The results indicate that standard free energy values are negative which mean that the reaction is spontaneous. The values of enthalpy of an adsorption process may be used to distinguish between physical and chemical adsorption [17]. Enthalpy change values range from 17.44 to 24.13 kJ/mol, based on this values adsorption of Fe(III) by RCC could be a physical adsorption process. Positive values of standard enthalpy change suggest that the process is endothermic nature. The standard entropy change values for the adsorption suggests a high degree of disorderness at the solid-liquid interface during the adsorption of Fe(III) onto RCC. This may be due to the adsorbed water molecules, which displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system [17].

3.5. Kinetics of adsorption studies

The pseudo first-order kinetic model was proposed by Lagergren.

The integrated form of the model is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Hence, a linear trace is expected between the two parameters, $\log(q_e - q_t)$ and t , provided the adsorption follows first order kinetics. The values of k_1 and q_e can be determined from the slope and intercept.

The adsorption may also be described by pseudo second-order kinetic model if the adsorption does not follow the first order kinetics. The linearised form of the pseudo second-order model [18] is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

A plot of t/q_t and t should give a linear relationship if the adsorption follows second order. q_e and k_2 can be calculated from the slope and intercept of the plot. Pseudo-first and second order kinetics

model was selected to describe the adsorption kinetics as shown in figure 2. The pseudo- first and second order kinetic parameters are evaluated in table 4. There is a good agreement between the calculated and experimental results were found in pseudo-second order model. The experimental data for the adsorption of Fe(III) with high correlation co-efficient ($r^2 = 1.0000$). It is also to be noted that the experimental adsorption capacities (q_e) are very close to the adsorption capacities calculated by the pseudo-second order kinetic model.

3.6. Intra particle diffusion

Weber and Morris suggested the following kinetic model to investigate the adsorption is intra-particle diffusion or not. According to this theory,

$$q_t = k_d \cdot t^{1/2}$$

A plot of q_t versus $t^{1/2}$ is given in the figure 3. The intra particle diffusion rate constant calculated from the slope of the linear portion of curves. The initial curve portions are shown to the boundary layer diffusion and the final linear portions shown to the intra-particle diffusion effect [19]. In figure 3, the linear portions of the curves don't pass the origin. This indicates that the mechanism of removal of Fe(III) by RCC is complex and both the surface adsorption as well as intra-particle diffusion contributes to the rate-determining step [20].

3.7. Effect of Co-ions

The effect of added co-ions like chloride ions, sulphates and nitrate ions were studied. The results indicate that the adsorption of Fe(III) is not much affected by the presence of other ions in solution. From this observation, the adsorbent is selective one towards to the Fe(III) [21].

3.8. FT-IR Studies

Numerous chemical functional groups like carboxyl, hydroxyl, amide, halogens etc have been identified as potential adsorption sites to be responsible for binding metallic ions to activated carbon [22]. FT-IR spectrum of activated carbon (Figure 4a) shows peak at 3367 cm^{-1} indicating the presence of hydroxyl group. The absorption peaks at 2923 cm^{-1} , $1623 - 1559 \text{ cm}^{-1}$, 1099 cm^{-1} and $760 - 656 \text{ cm}^{-1}$ corresponds to carboxylic, amides, halogens and amines. The region between $3000 - 2800 \text{ cm}^{-1}$ exhibits the C-H stretching vibrations of CH_3 and CH_2 functional groups [23]. FT-IR spectrum of loaded Fe(III) carbon shows in figure 4b, it can be seen that the main adsorption peaks of RCC activated carbon spectrum has not much changed compared to the spectrum of before adsorption. The results indicate that the adsorption process between RCC activated carbon and Fe(III) is a physical adsorption and not a complex reaction.

3.9. Scanning Electron Microscopic(SEM) Studies

The SEM micrograph clearly states the porous structure of the active carbon (figure 5a and figure 5b). There are holes and caves type openings on the surface of the specimen which would definitely have increased the surface area available for adsorption. The SEM micrograph of active carbon loaded with Fe(III) is shown on the figures. The figure shows evidence that the adsorbent structure was changed upon adsorbing the Fe(III) studied[24].

3.10. Effect of initial concentration

In this investigation, 50 mg of adsorbents (RCC and PPy/RCC) was treated with 50ml of Fe(III) solutions containing different concentration. Sorption experiments were carried out at the most suitable pH 4 for each sorbent. With increasing the initial concentration and the temperature, the removal of Fe(III) moderately increases in the case of RCC and PPy/RCC. Based on the results PPy/RCC is very efficient sorbent for removal of Fe(III) from aqueous solutions. The results are summarized in table 5.

3.11. Test with field samples

There are 10 water samples were collected from in and around Namakkal District. From that there are a few samples contain moderate heavy metals concentration, these samples were treated with RCC and PPy/RCC. After treatment, there is no heavy

metals concentration found in these water samples.(0.0000 ppm). The quality parameters of the treated water were in good agreement with the WHO and BIS standards.

4. CONCLUSIONS

Ricinus Communis seed shell activated carbons RCC, an agricultural waste, abundance, cheapness and environmentally friendly nature could be used as potential adsorbent for the removal of Fe(III) from aqueous solution contains heavy metals and polluted water. The Freundlich adsorption isotherm model describes the adsorption behaviour with good correlation co-efficient. The adsorption of Fe(III) was depended on the pH of the solution. Based on the results, the optimum contact time is 30 minutes and adsorbent dosage is 50 mg/L. Polypyrrole conducting polymer is the most important conducting polymer that can be synthesized chemical polymerization as coated form on the surface of RCC from aqueous solution. It was found that polypyrrole based conducting polymer was better adsorbent for removal Fe(III) compared to RCC from aqueous solution. The metal ion adsorption obeyed the pseudo-second order model based on the experimental and calculated q_e values. The removal of Fe(III) is simultaneously increased with increase in the temperature from 30 °C to 50 °C.

Table 1 - Characteristics of the RCC activated carbon

Parameter	Value
pH	7.70
pHzpc	5.86
Moisture Content (%)	3
Bulk density (g/ml)	0.4384
Solubility in water (%)	0.9273
Solubility in 0.25M HCl (%)	4.2334
Porosity (%)	70.935
Specific gravity	1.6367
Volatile matter (%)	4.54
Ash content	7.52
Fixed Carbon	84.94
Sodium (ppm)	62
Potassium (ppm)	2.8
Phenol adsorption capacity (%)	19.14
Conductivity (mS)	1.95
Surface area (m ² /g)	558

Table 2: Langmuir and Freundlich Isotherm constants

Adsorbent	Temp.(K)	Langmuir Constants				Freundlich Constants			
		Q _o	b	r ²	Sd	n	k	r ²	Sd
RCC	303	48.5437	0.3130	0.9742	0.0222	2.0554	12.4882	0.9848	0.0494
	313	51.020	0.3836	0.9846	0.0136	2.0383	14.2988	0.9945	0.0304
	323	54.0541	0.4591	0.9927	0.0072	1.9904	16.4058	0.9981	0.0184

Table 3: Thermodynamic parameters for the adsorption of Fe(III) onto RCC

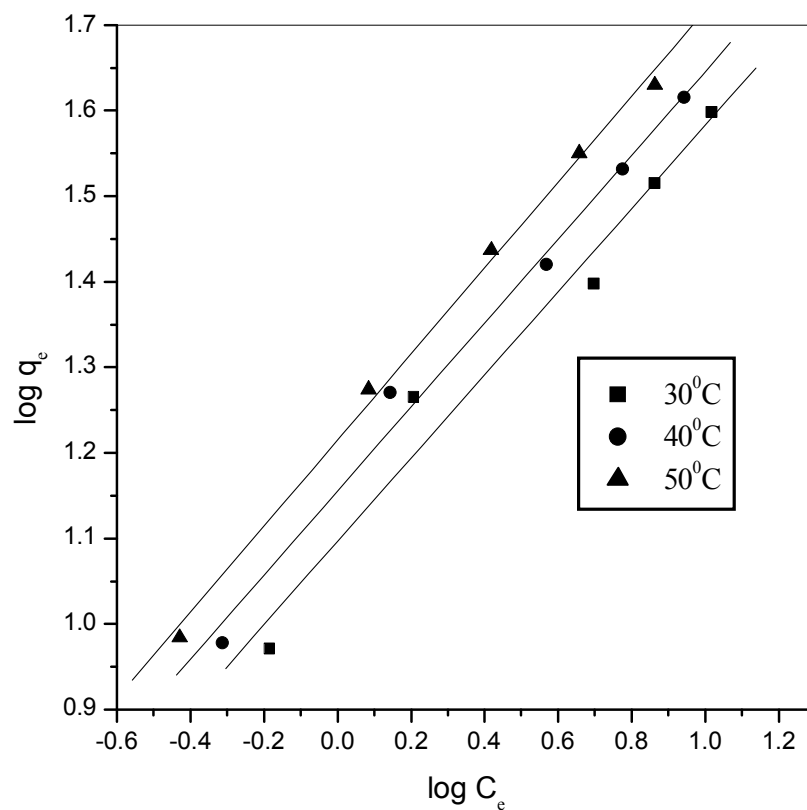
C _o , ppm	K			ΔG°(KJ mol ⁻¹)			ΔH° (KJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)
	30°C	40°C	50°C	30°C	40°C	50°C		
10	14.328	19.58	25.918	-6.7065	-7.7406	-8.7409	24.1318	101.7634
20	11.424	13.375	15.469	-6.1359	-6.7487	-7.3549	12.3278	60.9416
30	5.023	7.105	10.454	-4.0657	-5.1026	-6.3027	29.7944	111.657
40	4.478	5.7	7.802	-3.7767	-4.5294	-5.5170	22.5412	86.715
50	3.806	4.695	5.848	-3.3673	-4.0245	-4.7426	17.4437	68.6736

Table 4: Pseudo- first and second order parameters for Fe(III) Removal

Adsorbent	C _o , ppm	First order kinetic model					Second order model			
		q _e (exp) mg g ⁻¹	q _e (cal) mg g ⁻¹	k ₁ min ⁻¹	r ²	Sd	q _e (cal) mg g ⁻¹	k ₂ g mg ⁻¹ min ⁻¹	r ²	Sd
RCC	10	9.3476	0.4367	0.0969	0.9619	0.1091	9.3985	0.4697	0.9999	0.0066
	20	18.3902	2.8223	0.1308	0.9779	0.1109	18.7266	0.0928	0.9999	0.0056
	30	25.0187	2.4513	0.1403	0.9516	0.1795	25.2525	0.1179	0.9999	0.0034
	40	32.6982	1.6550	0.1232	0.9381	0.1804	32.8947	0.1566	0.9999	0.0018
	50	39.5973	1.3665	0.1356	0.9668	0.1422	38.9105	0.1201	1	0.0007

Table 5: Effect of the initial Fe(III) concentration on sorption by RCC and PPy/RCC.

C _o , ppm	% of Fe(III) Removal using RCC			% of Fe(III) Removal using PPy/ RCC		
	30°C	40°C	50°C	30°C	40°C	50°C
10	93.48	95.14	96.29	98.26	98.57	98.99
20	91.95	93.04	93.93	96.17	95.39	96.99
30	83.4	87.66	91.27	93.52	95.15	95.95
40	81.75	85.08	88.64	87.78	89.49	91.76
50	79.19	82.44	85.39	85.15	89.29	91.08

**Figure 1. Freundlich Adsorption Isotherm**

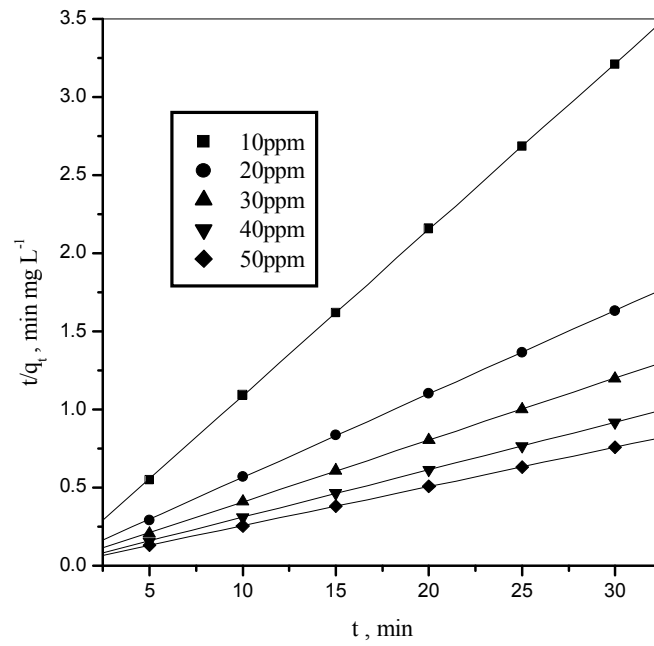


Figure 2. Second order kinetics model

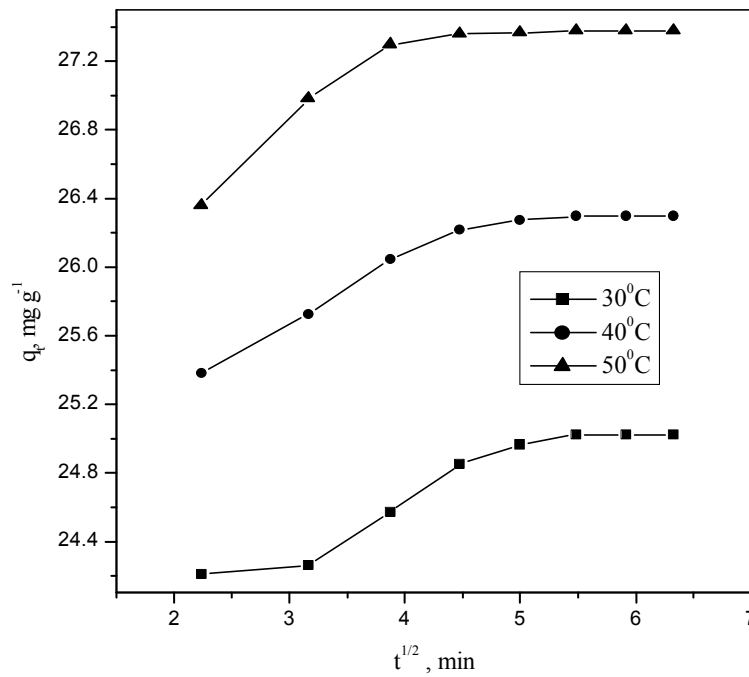


Figure 3. Intraparticle Diffusion Plot

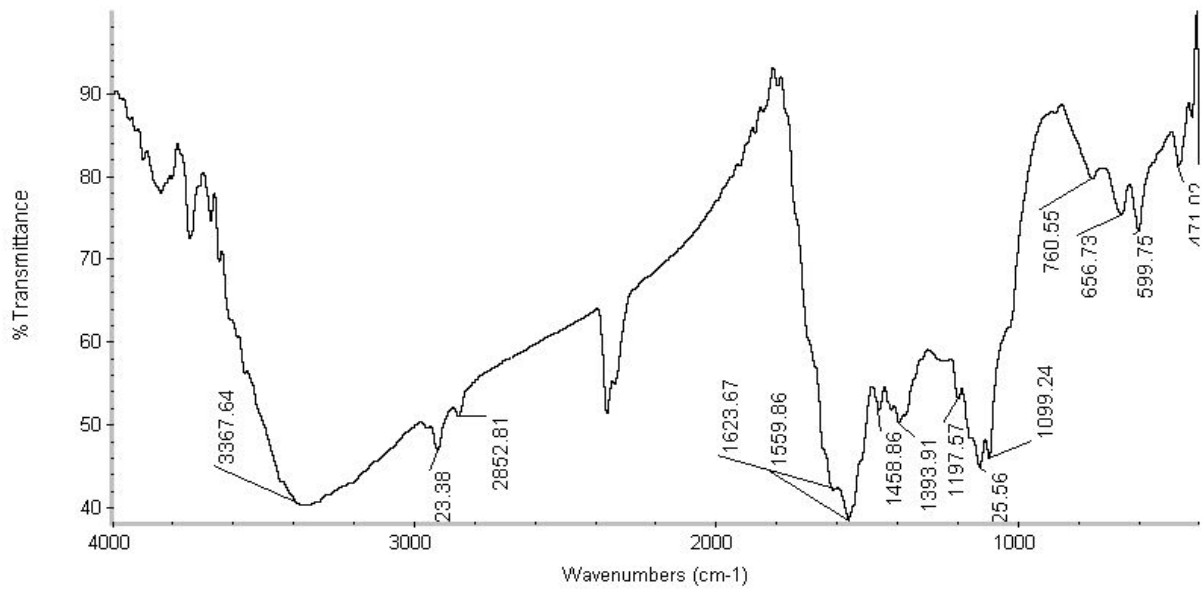


Figure 4a). The FT-IR spectrum of RCC activated carbon before adsorption

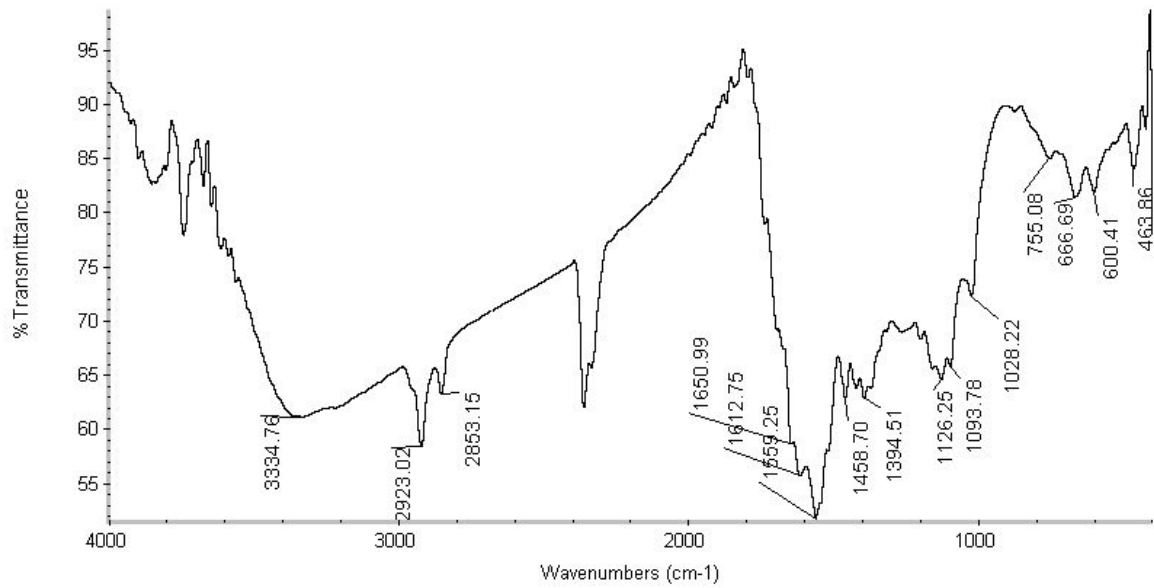


Figure 4b). The FT-IR spectrum of RCC activated carbon after adsorption

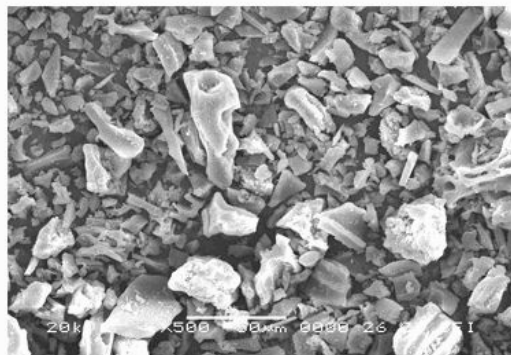


Fig 5a.SEM Photograph Before Adsorption

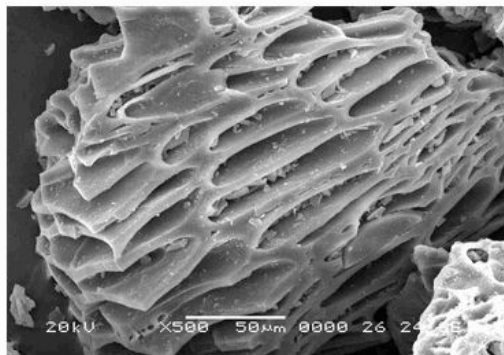


Fig.5b.SEM Photograph after Adsorption

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6. LIST OF SYMBOLS AND ABBREVIATIONS

RCC	Ricinus Communis Seed Shell activated carbon
PPy/RCC	Polypyrrole coated Ricinus Communis Seed Shell activated carbon
C_e	Adsorbate concentration at equilibrium time (mg L^{-1})
C_0	Initial concentration of adsorbate (mg L^{-1})
k_1	Lagergren first order rate constant (min^{-1})
k_2	Second-order adsorption rate constant ($\text{g mg}^{-1}\text{min}^{-1}$)
q_e	Amount of adsorbate adsorbed at equilibrium time (mg g^{-1})
Q_0	Langmuir adsorption capacity (Langmuir constant) (mg g^{-1})
R_L	Equilibrium parameter
K_d	Intraparticle diffusion rate constant.

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