



Removal of COD from Groundwater in and Around Industrial Areas-Using Activated Carbon Powder Prepared by Groundnut Foliage and Groundnut husk

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ABSTRACT

The following study explains that the adsorption efficiency of activated carbon used by Groundnut foliage and Groundnut husk for the deportation of COD (Chemical oxygen demand) from groundwater collected from in and around industrial areas of Vellore district was investigated with different activating conditions (Activating agent-KOH, ZnCl₂ and H₃PO₄; Impregnation ratio-1:1, 1:2, 1:2; and activation temperature-500-700°C. The activated carbon prepared based on optimized condition has well-developed pore structure and functional groups which is confirmed from SEM image and FTIR analysis respectively. The adsorption equilibrium was reached in 240 min with the isotherm data fitted well in both the model such as Langmuir model and Freundlich's model indicating chemisorption's adsorption for the activated carbon. Moreover, the adsorption process was exothermic accompanied by a decrease in irregularity. Furthermore, the adsorption kinetic study indicated that the adsorption process of the prepared sample follows the pseudo-second-order kinetic model compare to the pseudo-first-order kinetic model.

Keywords: Activated carbon, Adsorption, Groundnut foliage, Vellore district, Groundwater.

INTRODUCTION

Industrial and urban effluents are one of the main pollutants which can cause environmental pollution¹. Among the pollutants, sulfate is one of the significant inorganic pollutants found in urban effluents and with different amounts in industrial wastewaters; its concentration in lakes and seas is increasing quickly due to the urban and industrial

effluents drainage². The activated carbon used to remove of pollutants from waste water by adsorption method. It is one of the important methods to treat the industrial wastewater. To removal of highly dissolved substances from waste water by used activated carbon. The jack fruit peel activated carbon used to remove the dye industry of malachite green³. The activated carbon of agricultural waste used to remove the dye of methylene blue from



waste water⁴. The orange G dye removed using the spesiapopulnea activated carbon by adsorption method⁵. The date palm derived activated carbon used methodology of surface response⁶. The peanut shell activated carbon used to absorb the select metal ions⁷. The surface area of activated carbon of sunflower seed is 110.35-146.06 m²g⁻¹ which is used to removal of acid blue 8. 56% of dyes consumed in textile industry in the world per annum⁹⁻¹⁰. Most of the methods are having advantages and disadvantages for the removal of dye from wastewater¹¹. Using activated carbon in adsorption process is one of the effective and economic potential methods for the removal of dyes from the wastewater¹²⁻¹⁵.

Any carbon material can be used to produce activated carbon. Up to now, several studies have been conducted using activated carbon derived from agricultural wastes such as peanut crust, nuts shell, tamarind shell, peanut shell, 16 rice bran, rice hulls, banana peel, orange peel, apple peel, hazelnut, walnut shell, tree's leaf and bark, oak essence, cane bagasse, corn, wheat bran, sawdust, sunflower stem, grape stem, modified algae, alfalfa and mustard¹⁶ for the removal of pollutants from wastewater.

In this study, the activated carbon powder obtained from Groundnut foliage and groundnut husk were used to remove COD from groundwater samples and following parameters were analyzed such as contact time, pH, temperature and adsorbent concentration in aqueous solution. The optimum operational conditions for getting maximum adsorption was obtained the adsorption was analyzed by Freundlich's adsorption isotherm for water and waste water treated by activated carbon due to high rate and capacity.

MATERIALS AND METHODS

In this experiment used material in activated carbon from groundnut foliage and

groundnut husk. The groundwater samples were collected from bore wells located in residential areas of Vellore district using clean polythene bottles and it's preserved in refrigerator. According to world health organization and ISI standard used to analyses the samples¹⁸. The double distilled water is used to prepare the all reagents.

Activated Carbon

The sample of impregnated groundnut foliage and husk were activated in furnace of muffle at 650-700°C respectively for 1 h then cooled at room temperature. The cold water, acid or base used to wash the activated sample then followed by double distilled water used to remove the Surplus chemical agent. The cleaned samples dried in oven at the temperature range of 80±5°C for 24 hours. After carbonization, the activated carbon turned to powder by milling and graded through sieve No.25, then stored inside anti-moisture plastic bottles. The scanning electron microscope (SEM) used to analyze its morphology.

Adsorptions of contaminants

The study of adsorption equilibrium was carried out by using granular activated carbon, produced of mass 3, 5, 7 and 9 g. Each mass was placed in 250 mL of Erlenmeyer flask contains 100 mL of waste water. Each flask was shaken continuously for 3 hours. The percolation of activated carbon with effluent of waste water until equilibrium was achieved. Five minutes interval the mixture was taken and filtered, the determination of COD in filtrate. To achieved removal of organic compounds by varying dosages of activated carbon as well as solid fluid phase equilibrium type. The data of equilibrium obtained, processed adsorption of contaminated in activated carbon using adsorption isotherm such as Langmuir and Freundlich, which are commonly used in water treatment.

Table 1: Classical method of prepared activated carbon

Biomass	Reagent	Impregnation Ratio	Temperature(°C)	Impregnation Time (h)	Activation Time (h)
GFAC & GHAC	KOH	1:1	700	24	1
	ZnCl ₂	1:2	700	24	1
	H ₃ PO ₄	1:3	700	24	1

Note: GFAC-Groundnut foliage activated carbon GHAC-groundnut husk activated carbon

RESULTS AND DISCUSSION

Characterization of Activated Carbon (GHAC & GFAC)

The physical characteristics of activated carbons prepared from groundnut husk and groundnut foliage are shown in Table 1. Bulk density of groundnut husk activated carbon (GHAC) is lower as compared with groundnut foliage activated carbon (GFAC) because of its powdered nature. Percentage loss on ignition is higher for groundnut foliage activated carbon indicating its high carbon content. Surface area is very high in case of groundnut husk activated carbon due to its small particle size, which shows the possibility of high adsorptive nature. On comparison with the GHAC and GFAC, the GHAC possess less adsorption capacity.

Table 2: Bulk densities of groundnut foliage and groundnut husk activated carbon

S.no	Activated carbon	Bulk density (mg/cc)
1	GFAC	0.260
2	GHAC	0.206

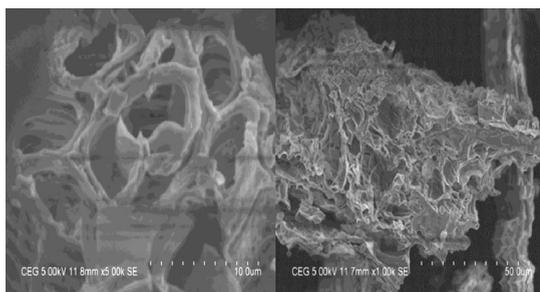


Fig. 1(a). SEM image of GFAC

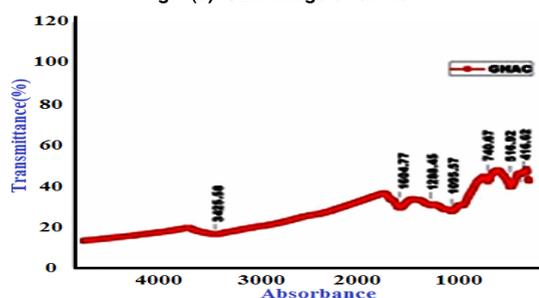


Fig. 2(a). FTIR Analysis of GFAC

Table 3: FTIR analysis of GFAC

S.no	Frequency(cm ⁻¹)	Functional group	Intensity
1	3985	-OH	Medium
2	3425	-OH	Medium
3	1602	-C=O	Strong
4	1288	-COOH	Medium
5	1090	Ether C-O	Strong
6	744	PO ₄	Strong and Sharp
7	412	N-containing bio-ligand	Strong and Sharp

Scanning electron microscope (SEM)

The surface morphology of activated carbon is prepared using the groundnut foliage and husks are depicted in Fig. 1(a) and Fig. 1(b) respectively. SEM images of adsorbents were taken to know the pores and cavities for effective adsorption for the adsorbent. The more pores and cavities clearly showed that the higher possibility of COD to be occupied and adsorbed into pores of groundnut foliage than the groundnut husk.

Fourier transform infrared spectroscopy(FTIR)

The FTIR spectroscopy analysis of groundnut husk activated carbon was made in the range of 4800 to 415 cm⁻¹ region (Fig. 2(a) & 2(b)).

The functional groups which represent surface functionality of the groundnut foliage and groundnut husk activated carbons were listed in Table below (Table 3 & 4).

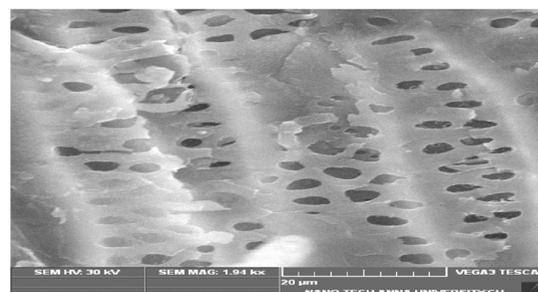


Fig. 1(b). SEM image of GHAC

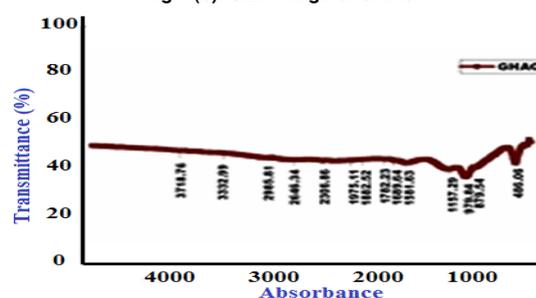


Fig. 2(b). FTIR Analyses GHAC

Table 4: FTIR analysis of GHAC

S.no	Frequency(cm ⁻¹)	Functional group	Intensity
1	3718	-OH	Medium
2	3330	-OH	Medium
3	2982	Alkaline C-H	Medium
4	1680	-C=O	Strong
5	1582	-COOH	Medium
5	1157	Ether C-O	Strong
6	980	PO ₄	Strong and Sharp
7	488	N-containing bio-ligand	Strong and Sharp

Effect of pH

The pH of groundwater is one of the important factors for the chemical oxygen demand removal using activated carbons. The highest level of COD removal was detected at pH 6 for the both activated carbons. Above this pH range level the removal percentage is decreased from 69% to 66% and 58% to 55% on activated carbon of groundnut foliage and groundnut husk respectively. It is evident that the optimum pH for the removal of COD is 6.

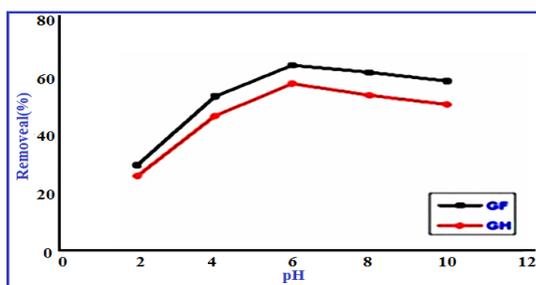


Fig. 3. Effect of pH on COD removal

Effect of Contact Time on the adsorption process

The reaction of activated carbon of groundnut foliage and groundnut husk with different time interval on COD removal is shown in Fig. 4. Around 80% & 68% of COD removal takes place in 240 min for activated carbon of groundnut foliage and groundnut husk respectively. The equilibrium was reached after 240 minute. The change in the rate of adsorption could be due to fact that initially all the adsorbent sites are vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of empty sites of adsorbent & COD concentrations (Fig. 4). Adsorption rate decreases showed particularly, termination of the trials. This can be clearly indicated that the absence of available active site is mandatory for the further adsorption after reaching the equilibrium. The Experimental data clearly shows that groundnut foliage of activated carbon gives the better result of COD adsorption than the groundnut husk activated carbon.

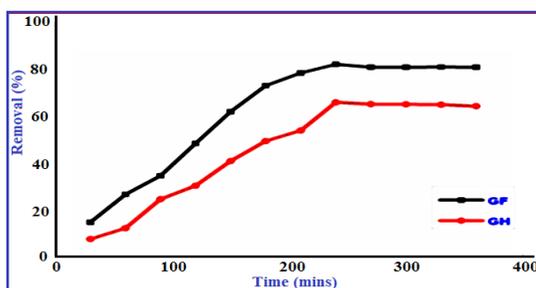


Fig. 4. Effect of time on COD

Effect of Adsorbent Dosage on adsorption

The sequence of adsorption experimentations were approved out with different dosages of carbon on the removal of chemical oxygen demand varying from 0.1 g-0.7 g to 50 mL at the concentration of 150 ppm. The carbon dosage for the adsorption of COD through groundnut foliage and husk of activated carbon was started to increase (39% to 93% and 36% to 78% respectively) by increasing the adsorbent dose, owing to the rise of the activated site open for the adsorption. The removal percentage increased sharply with an increase in the adsorbent concentration from 0.1 g to 0.5 g/100 mL. There is no effective changes in removal efficiency were observed after the concentration level of 0.5 g/100 mL adsorbent dosage. If 0.5 g/100 mL is considered, the optimal dose for other loadings (Figure 5).

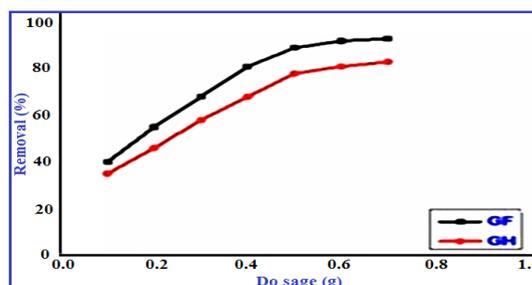


Fig. 5. Effect of adsorbent dosage on COD

Adsorption Isotherm Modeling

In Fig. 6(a) and 6(b) Modeling shows that adsorption of chemical oxygen demand of Freundlich's and Langmuir isotherm onto optimized activated carbon of groundnut foliage and groundnut husk respectively. The isotherm denotes specific relation among concentration of adsorbate and its degrees to addition on adsorbent surface. (Table 5) It has exposed that, the values of coefficient in Freundlich's isotherm ($R^2 = 0.9913$ and $R^2 = 0.991$) was higher than the Langmuir isotherm ($R^2 = 0.9672$ and $R^2 = 0.9767$) on groundnut foliage and husk of activated carbon respectively. It's confirmed that, the isotherm data better fitted in the Freundlich's equation than Langmuir equation¹⁰. The data derived from the experiment for adsorption of chemical oxygen demand on activated carbon have been fitted both the model such as Langmuir and Freundlich. But small values of correlation Co-efficient showed that Langmuir model is less fitted current adsorption compared with Freundlich's model for both the activated carbon. In common, according to R^2 standard, Freundlich's model fits improved for COD adsorption for existing adsorption study (Table 5, 6 & 7).

Table 5: Langmuir and Freundlich's constant for COD adsorption

Activated Carbon	Langmuir Constant		Freundlich's Constant	
	K (mg/g)	R ²	lnKF	R ²
Groundnut Foliage	50	0.9672	4.2	0.9913
Groundnut Husk	0.07	0.9767	5.2	0.991
Lecus Aspera	2.53	0.77	3.51	0.90

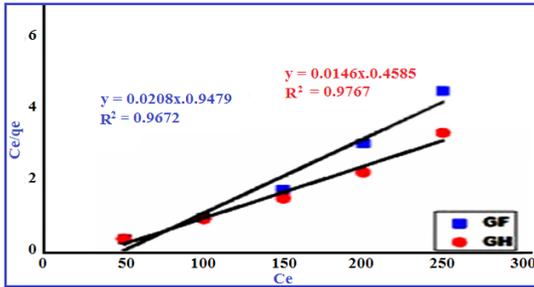


Fig. 6(a). Langmuir's isotherms of GFAC & GHAC

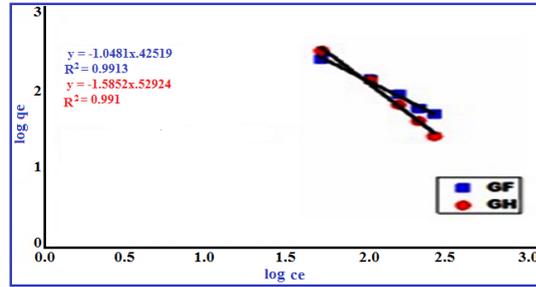


Fig. 6(b). Freundlich's isotherms of GFAC & GHAC

Table 6: Pseudo-first orders and Pseudo-second order kinetic model constant for COD adsorption of GFAC

Adsorbate (GF) (mg/L)	Pseudo-first order kinetic			Pseudo-second order kinetic		
	K ₁ (min) ⁻¹	q _e (mg/g)	R ²	K ₂ (min) ⁻¹	q _e (mg/g)	R ²
50	0.036	1.87	0.893	112.3	0.0089	0.995
100	0.028	2.16	0.899	105.26	0.0095	0.991
150	0.026	2.31	0.896	113.6	0.0088	0.992
200	0.023	2.40	0.909	95.23	0.0105	0.963
250	0.033	2.54	0.920	113.6	0.0088	0.960

Table 7: Pseudo-first orders and Pseudo-second order kinetic model constant for COD adsorption of GHAC

Adsorbate (GF) (mg/L)	Pseudo-first order kinetic			Pseudo-second order kinetic		
	K ₁ (min) ⁻¹	q _e (mg/g)	R ²	K ₂ (min) ⁻¹	q _e (mg/g)	R ²
50	0.032	1.88	0.873	119.87	0.0091	0.991
100	0.029	2.18	0.919	101.67	0.0098	0.934
150	0.025	2.38	0.898	117.42	0.0086	0.997
200	0.021	2.42	0.919	96.87	0.0108	0.973
250	0.037	2.58	0.928	119.2	0.0085	0.971

The regression coefficient of above 0.99 is considered to be important factor and from figure (Fig. 6a) and (Fig. 6b) respective coefficients were calculated and found the adsorption follows pseudo-second-order kinetic model which confirms the chemisorption's of COD on both the activated carbon of groundnut foliage and husk.

CONCLUSION

The present study involves the preparation of activated carbon using groundnut foliage material by chemical activation method with different activating conditions (Activating agent- KOH, ZnCl₂

and H₃PO₄; Impregnation ratio-1:1, 1:2, 1:2; Activation temperature-500-700°C). Experimental results and predicted values were well fitted in the quadratic model. The groundnut foliage activated carbon (GFAC) prepared based on optimized condition has well-developed pore structure and functional groups which is confirmed from SEM image and FTIR analysis respectively. The adsorption equilibrium was reached in 240 min with the isotherm data fitted well in Langmuir model and Freundlich's model indicating chemisorptions for the activated carbon. Equilibrium with R² value higher than Langmuir isotherm data that confirms the system follows Freundlich's model. From the experimental

data specify that the prepared sample having good surface area for the COD removal. A result shows that it is very much evident that the prepared activated carbon (GFAC and GHAC) possess the very good ability to remove organic waste from water.

Conflict of Interests

The authors declare that there is no conflict of interests.

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