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Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat

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Abstract

Activated carbon prepared from rubber seed coat (RSCC), an agricultural waste by-product, has been used for the adsorption of phenol from aqueous solution. In this work, adsorption of phenol on rubber seed coat activated carbon has been studied by using batch and column studies. The equilibrium adsorption level was determined to be a function of the solution pH, adsorbent dosage and contact time. The equilibrium adsorption capacity of rubber seed coat activated carbon for phenol removal was obtained by using linear Freundlich isotherm. The adsorption of phenol on rubber seed coat activated carbon follows first order reversible kinetics. The suitability of RSCC for treating phenol based resin manufacturing industry wastewater was also tested. A comparative study with a commercial activated carbon (CAC) showed that RSCC is 2.25 times more efficient compared to CAC based on column adsorption study for phenolic wastewater treatment. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Activated carbon; Rubber seed coat; Adsorption; Phenol; Wastewater

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1. Introduction

Aromatic compounds such as phenols occur in wastewater of a number of industries such as high temperature coal conversion, petroleum refining, resin and plastics. Such aromatic hydroxy compounds can be toxic when present in elevated levels and are known or suspected

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to be carcinogens [1]. Thus, the removal of such chemicals from industrial effluents is of great importance.

Current methods for removing phenolics from wastewater include microbial degradation, adsorption on activated carbon, chemical oxidation (using agents such as ozone, hydrogen peroxide or chlorine dioxide), incineration methods, solvent extraction and irradiation [2–5]. The choice of system depends on economic and other factors.

The high cost of activated carbon has stimulated interest in examining the feasibility of using cheaper raw materials. Substitute materials tested include straw, auto mobile tyres, fly ash, coal reject, sewage sludge, bagasse, fertilizer waste and saw dust [6–11]. Because of the high cost and variable performance of carbon regeneration, single use materials are desirable [12]. Phenols are particularly susceptible to irreversible adsorption on to some activated carbons [13,14]. Moreover, as pointed out in the paper by Streat et al. [6], the highly porous structure of activated carbon may represent over design for many applications in water treatment. It may be sufficient to use a larger dose of the less expensive substituted and achieve the same treatment goal.

Many reports have appeared on the development of activated carbon from cheaper and readily available materials [15]. Activated carbons derived from pine bark [16] and apricot stone [17] have been successfully employed for the removal of phenol from aqueous solutions. We have recently reported that activated palm seed coat carbon removed phenol, *p*-chlorophenol and *o*-cresol efficiently from aqueous solutions [18–20]. Rubber seed coat, a waste agricultural by-product, is utilized in South India as fuel and manure. The investigation reported here deals with a comparative study of RSCC and CAC for the removal of phenol from aqueous solution and from a phenolic-based resin manufacturing industry wastewater.

2. Experimental

2.1. Preparation of activated carbon

Activated carbon from rubber seed coat (*Hevea brasiliensis*) was prepared by the procedure reported by Rengaraj et al. [21,22]. Initially, the materials were washed thoroughly with water to remove earthy matter and dried at 110°C. The dried material was carbonised with dolomite at 500°C for 3 h. The carbonised material was washed well with dilute hydrochloric acid and water to remove dirt and dried at 110°C. The dried material was subjected to thermal activation in a carbon dioxide atmosphere at 850–900°C for 30 min. The materials were ground in an agate mortar and the particles having an average diameter of ∼0.5 mm (20–50 mesh ASTM), were taken for further studies.

2.2. Characterisation of activated carbon

Activated carbon was characterized by adopting the standard procedures [23–25]. The moisture content of the carbon was determined by heating a known weight of the sample in an air oven maintained at 105 ± 5°C for about 4 h. The residue was ignited in a muffle furnace at 1000°C for about 3 h to determine the ash content. Iron in the ash content was

Table 1
Characteristics of rubber seed coat carbon (RSCC) and commercial activated carbon (CAC)

S. no.	Control tests	RSCC	CAC
1	Bulk density (ml)	0.70	0.68
2	Moisture content (%)	14.52	12.57
3	Ash content (%)	0.93	2.91
4	Fixed carbon content (%)	99.07	97.09
5	Matter soluble in water (%)	1.16	1.55
6	Mater soluble in acid (%)	1.92	4.58
7	pH	8.10	9.2
8	Decolourising power (mg/g)	83.2	73.5
9	Phenol number (mg)	9.02	5.15
10	Ion exchange capacity (mg/g)	Nil	Nil
11	Surface area (m^2/g)	598	296
12	Iron content (%)	Nil	Nil

estimated by atomic absorption spectrophotometer (Perkin-Elmer-2380). Freshly boiled water was digested with dried carbon and pH was determined for the clear solution using a pH meter (Systronics-335). Decolourising power of the carbon was determined using a methylene blue solution. The amount of carbon required for 90% removal of phenol was taken as the phenol number. Surface area measurement was carried out using Micromeritics Pulse Chemisorb 2700 equipment. The characteristics of the activated carbon are presented in Table 1.

2.3. Batch experiments

A 100 ml each of phenol solution (25 mg/l) adjusted to different pH values were placed in 250 ml leak-proof reaction bottles and a known amount of rubber seed coat carbon was added to each bottle. The solution was equilibrated for 24 h at 27 ± 1°C in a mechanical shaker. After the equilibration period, the carbons were filtered and analysed for phenol following the standard colorimetric procedure [23]. Desorption studies were conducted using dilute sodium hydroxide solution by providing an equilibration time of 24 h. Kinetic experiments were conducted using a known weight of carbon dosage and employing phenol concentration in the range of 10–30 mg/l. After regular intervals of time, suitable aliquots were analysed for phenol concentration and recorded. The rate constants were calculated by using the conventional rate expression [26].

2.4. Column experiments

Column experiments were performed in a glass column of 2.5 cm diameter. The known amount of the carbons under study were made into a slurry with distilled water. The slurry was transferred slowly into the glass column packed at the bottom with glass wool. After complete transfer of carbon, the bed was washed several times with water. The phenol solution was stored in a polythene container of 5 l capacity fitted with a tap at the bottom to which a polythene tube was connected. The other end of the tubing was connected to a glass socket containing a flow regulating valve. The outlet of the valve fixed to the top of the column had a provision to connect a peristaltic pump to control the flow rate. For all column experiments, a pressure head of 10–15 cm was maintained over the carbon beds. A constant flow rate was maintained for each experiment. Frequent checks were made at the interval of 10 min to correct for any change in the flow rate. Lot volumes ranging from 100 to 10,000 ml were collected separately. Each lot was analysed for phenol by 4-aminoantipyrine analytical procedures using suitable aliquots [23].

3. Results and discussion

The adsorbent prepared from rubber seed coat was studied for the removal efficiency of phenol from aqueous solution under different experimental conditions. The experimental results and the relevant observations are discussed in the following sections.

3.1. *Effect of carbon dosage*

Fig. 1. shows the amount of phenol removed as a function of carbon dosage at their solution pH (6.2). Carbon dosage was varied from 0.5 to 10 g and equilibrated for 24 h. It is evident that for the quantitative removal of 25 mg/l of phenol in 100 ml, a minimum carbon dosage of 2.5 g RSCC and 3.0 g of CAC is required for 96% removal of phenol. The data

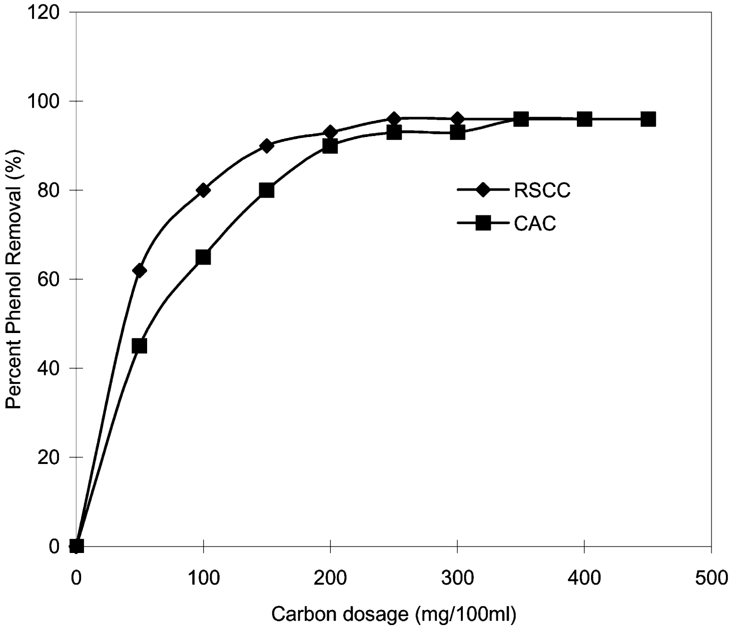

Fig. 1. Effect of carbon dosage on the removal of phenol by RSCC and CAC system (initial concentration of phenol = 25 mg/l; pH = 6.2; equilibration time = 24 h).

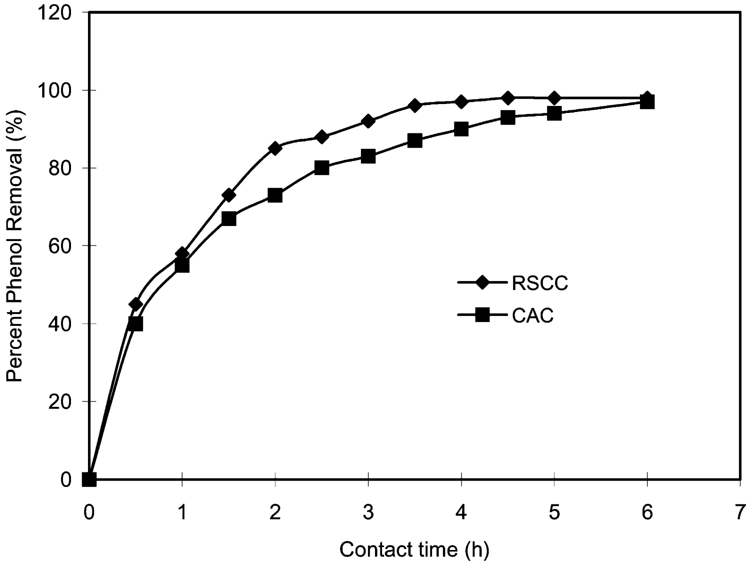

Fig. 2. Effect of contact time on the removal of phenol with RSCC and CAC system. (initial concentration of phenol = 25 mg/l; pH = 6.2; carbon dosage, RSCC = 2.5 g/l and CAC = 3.0 g/l).

clearly shows that the RSCC is more effective than CAC for the removal of phenol. The results also clearly indicate that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible [18–20].

3.2. Effect of contact time

Fig. 2 shows the effect of contact time on the removal of phenol by RSCC and CAC. Known volume of phenol in the solution pH with optimum carbon dosage was kept in the mechanical shaker and equilibrated for the period ranging from 0.25 to 24 h. The experimental adsorption rate curve for phenol is shown in Fig. 3. The removal increases with time and attains equilibrium in 3 h for RSCC and 6 h for CAC for initial phenol concentration of 25 mg/l. This indicates that RSCC would require less residence time for the complete removal of phenol compared to CAC. The equilibrium time was independent of initial concentration of phenol. The phenol removal versus time curves are single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of phenol on the surface of the adsorbent [27].

3.3. Desorption of phenol

Desorption studies help elucidate the mechanism of adsorption and recover the precious phenols, water and the adsorbent. Attempts were made to desorb phenol from the spent carbons using hydrochloric acid and sodium hydroxide of various strengths. From this, sodium hydroxide has been found to be good reagent for the desorption of phenol from

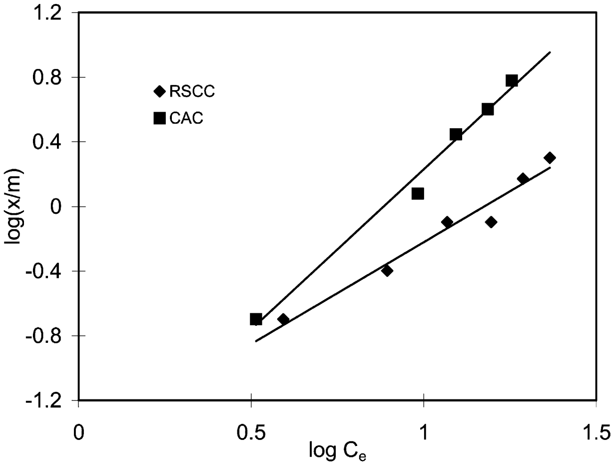

Fig. 3. Freundlich adsorption isotherm for RSCC and CAC with phenol system.

RSCC and CAC. This may be attributed to the formation of sodium salt of phenol which may facilitate the desorption of phenol from the carbon surfaces [18–20]. From the studies it was found that approximately 0.1 and 0.14 N NaOH is required for quantitative desorption of phenol from RSCC and CAC, respectively.

3.4. Adsorption isotherm

The equilibrium removal of phenol was mathematically expressed in terms of adsorption isotherms. The Freundlich adsorption isotherm was applied for the adsorption of phenol by RSCC and CAC. The experimental results obtained for the adsorption of phenol on RSCC and CAC at room temperature (25 ± 1°C) and at optimum conditions of pH, contact time and dose of adsorbent were found to obey Freundlich adsorption isotherm [28].

$$\left(\frac{x}{m}\right) = kC_{\mathrm{e}}^{1/n}$$

The logarithmic form of the equation becomes

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C_{\mathrm{e}}$$

Freundlich adsorption isotherm represents the relationship between the amounts of cobalt adsorbed per unit mass of the adsorbent (x/m) and the concentration of the phenol at equilibrium (C_e). The constants K and n represent the adsorption capacity and intensity of adsorption, respectively. The data obtained in this study fit in Freundlich adsorption isotherm (Fig. 3).

The plot of log (x/m) versus log C_e for various initial concentrations is found to be linear, indicating the applicability of classical adsorption isotherm to this adsorbate–adsorbent system. The adsorption capacity (k) is found to be 15.5 and 9.94 mg/g and adsorption intensity (n) is found to be 1.3 and 3.5 for RSCC and CAC, respectively. Higher value for k indicates higher affinity for cobalt and the values of n lie between 1 and 10 indicating favorable adsorption [29].

3.5. Adsorption kinetics

Kinetics of adsorption describe the solute uptake rate which in turn governs the residence time of adsorption reaction. It is one of the important characteristics in defining the efficiency of adsorption. Hence, in the present study, the kinetics of phenol removal has been carried out to understand the behaviour of this adsorbent. The adsorption of phenol from an aqueous solution follows a reversible first order kinetics, when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the phenolic solution and the activated carbon may be expressed as,

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \tag{1}$$

where k_1 is the forward reaction rate constant and k_2 the backward reaction rate constant.

If 'a' is the initial concentration of phenol and 'x' the amount transferred from liquid phase to solid phase at any time t, then rate is given by,

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{-\mathrm{d}(a-x)}{\mathrm{d}t} = k(a-x) \tag{2}$$

or

$$k = \frac{1}{t} \ln\left(\frac{a}{a-x}\right) \tag{3}$$

where k is the overall reaction rate constant. Since k_1 and k_2 are the rate constants for the forward and reverse process, the rate can be expressed as,

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1(a-x) - k_2 x \tag{4}$$

If X_e represents the concentration of phenol adsorbed at equilibrium, then at equilibrium,

$$k_1(a - X_\mathrm{e}) - k_2 X_\mathrm{e} = 0$$

because under these conditions,

$$\frac{\mathrm{d}x}{\mathrm{d}t} = 0 \quad \text{or} \quad k_\mathrm{C} = \frac{X_\mathrm{e}}{a - X_\mathrm{e}} = \frac{k_1}{k_2} \tag{5}$$

where k_C is the equilibrium constant, which plugging into Eq. (4) yields

$$\frac{\mathrm{d}x}{\mathrm{d}t} = (k_1 + k_2)(X_\mathrm{e} - x) \tag{6}$$

The above equation of the form $\mathrm{d}x/\mathrm{d}t = k(a-x)$

Therefore, integration of the equation lead to

$$k_1 + k_2 = \frac{1}{t} \ln \left(\frac{X_e}{X_e - x} \right) \tag{7}$$

The above equation can be written in the form of

$$\ln(1 - U_t) = -(k_1 + k_2)t = -kt \tag{8}$$

where $U_t = x/X_e$ and k is the overall rate constant.

Further,

$$k = k_1 + k_2 = k_1 + \frac{k_1}{k_C} = k_1 \left[1 + \frac{1}{k_C} \right] \tag{9}$$

U_t can be calculated using the expression

$$\frac{C_{A(0)} - C_{A(t)}}{C_{A(0)} - C_{A(e)}} = \frac{x}{X_e} = U_t \tag{10}$$

where $C_{A(0)}$ is the initial concentration of phenol, $C_{A(t)}$ the concentration of phenol present at any time (t), $C_{A(e)}$ the concentration of phenol present at equilibrium condition and U_t is called the fractional attainment of equilibrium of phenol and was calculated by considering phenol adsorption over the activated carbon in a given time range 1–24 h. In the present study, a concentration of phenol over the range 10–30 mg/l was tried. Using the kinetic equations, the overall rate constant, the forward and backward rate constants were calculated. For instance, by plotting $\ln(1 - U_t)$ verses t (Fig. 4a and b) the overall rate constant 'k' for a given concentration of phenol was calculated by considering the slope of straight line in the Fig. 4a and b and by using Eqs. (5) and (8) the equilibrium constant k_C, forward and backward rate constants k_1 and k_2 were calculated and shown in Table 2 [26]. From Table 2, it could be seen that the forward rate constants for the removal of phenol were much higher than the backward rate constants namely in the desorption process [30].

In order to assess the nature of the diffusion process responsible for adsorption of phenol on RSCC and CAC, attempts were made to calculate the co-efficients of the process. If film

Table 2
Rate constants for the removal of phenol by rubber seed coat carbon (RSCC) and commercial activated carbon (CAC)

Name of the carbon	Phenol concentration (mg/l)	Overall rate constant $K = k_1 + k_2$ (h^{-1})	Forward rate constant k_1 (h^{-1})	Backward rate constant k_2 (h^{-1})
RSCC	10	2.0645	2.0232	0.4129
	20	1.1629	1.1396	0.0232
	30	1.1233	1.0933	0.0299
CAC	10	1.2010	1.1769	0.0240
	20	0.8710	0.8620	0.0090
	30	0.7050	0.7003	0.0047

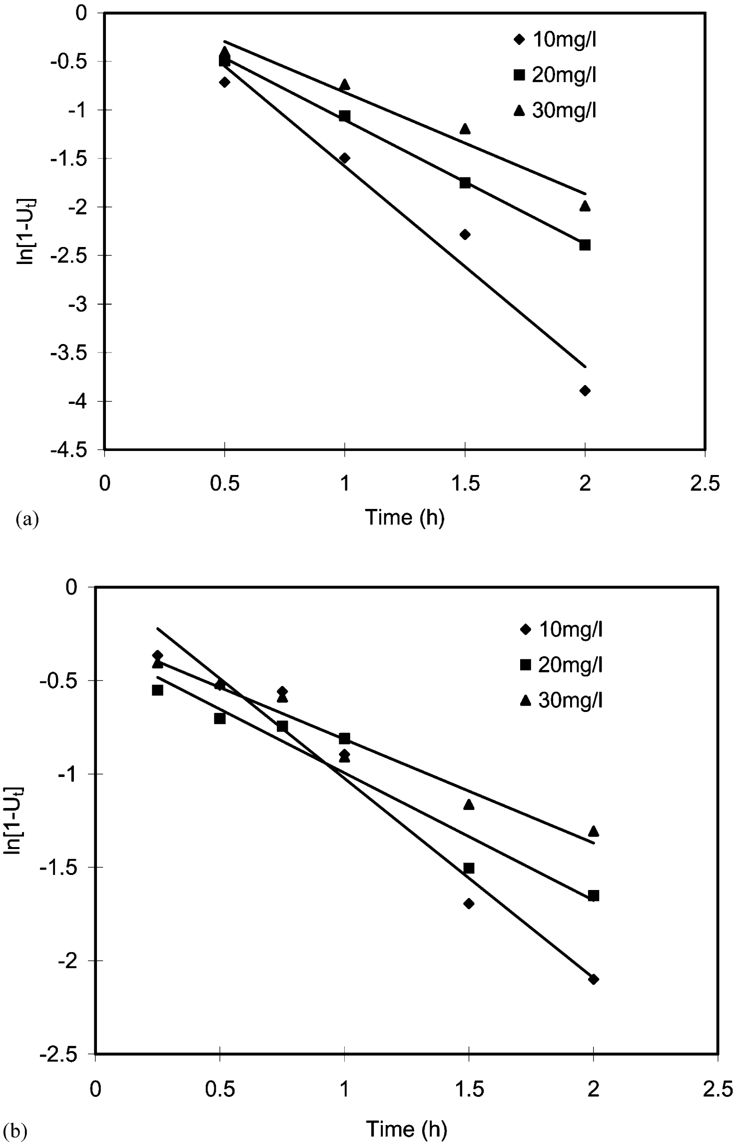

Fig. 4. (a) Kinetic fits for the adsorption of phenol and RSCC system. (b) Kinetic fits for the adsorption of phenol and CAC system.

diffusion is to be the rate determining step in the adsorption of phenol on RSCC and CAC surface, the value of film diffusion co-efficient (D_f) should be in the range 10^{-6} to 10^{-8} cm^2 s^{-1}. If pore diffusion is to be rate limiting, the pore diffusion co-efficient (D_p) should be in the range 10^{-11} to 10^{-13} cm^2/s [31]. Assuming spherical geometry for the adsorbent, the overall rate constant of the process can be correlated to the pore diffusion co-efficient and film

Table 3
Diffusion co-efficients for the removal of phenol by rubber seed coat carbon (RSCC) and commercial activated carbon (CAC) system

Name of the carbon	Phenol concentration (mg/l)	Film diffusion co-efficient (cm^2/s)	Pore diffusion co-efficient (cm^2/s)
RSCC	10	0.5362×10^{-8}	2.0519×10^{-8}
	20	0.3020×10^{-8}	1.1558×10^{-8}
	30	0.2897×10^{-8}	1.1164×10^{-8}
CAC	10	0.2749×10^{-8}	1.0522×10^{-8}
	20	0.2502×10^{-8}	0.9491×10^{-8}
	30	0.1557×10^{-8}	0.6076×10^{-8}

diffusion co-efficient independently in accordance with the expressions [26].

$$\text{pore diffusion co-efficient}: \quad D_\text{p} = 0.03 \times \frac{r_\text{o}^2}{t_{1/2}}$$

$$\text{film diffusion co-efficient}: \quad D_\text{f} = 0.23 \times \frac{r_\text{o}\partial}{t_{1/2}} \times \frac{\bar{c}}{c}$$

where r_o is the radius of the adsorbent (cm), ∂ the film thickness, $\bar{c}$ the amount adsorbed and c is the initial concentration. Employing the appropriate data and the respective overall rate constants, pore and film diffusion co-efficients for various concentrations of phenol were calculated for RSCC and CAC. The results are presented in Table 3. It is evident that the removal of phenol follow film diffusion process since the co-efficient values are in the range 10^{-6} to 10^{-8} cm^2/s for RSCC and CAC.

3.6. Test with phenolic-based resin manufacturing industry wastewater

The use of rubber seed coat activated carbon in the removal of phenolics from live wastewater was attempted by column studies in order to assess the suitability and acceptability of these carbons for commercial exploitations. The wastewater was collected from a phenolic-based resin manufacturing industry in Chennai, India. The physico-chemical characteristics of phenolic-based resin manufacturing industry wastewater are shown in Table 4. At optimum flow rate and bed height, the adsorption capacities for RSCC and CAC is 56 and 27 mg/g for synthetic phenolic solution and 36 and 16 mg/g for live phenolic wastewater, respectively. The efficiency of these carbons towards the removal of phenol in synthetic wastewater is higher than that of live phenolic effluents. The difference in the quantity of removal between synthetic and industrial wastewater is due to the presence of other competing impurities present in live wastewater which may interfere in the adsorption process. Also, this study indicates that the RSCC is much more effective compared to CAC with respect to the application to phenolic-based resin manufacturing wastewater.

Table 4
Physico-chemical characteristics of resin manufacturing phenolic wastewater

S. no.	Characteristics	Values
1	pH	7.4
2	EC (μS/cm)	285
3	Sulphate (mg/l)	60
4	Chloride (mg/l)	53
5	TDS (mg/l)	235
6	COD (mg/l)	487
7	BOD (mg/l)	60
8	Phenol (mg/l)	122

4. Conclusion

Rubber seed coat, an agricultural waste of India, is a potential source for the preparation of activated carbon. The characterisation studies reveals its adsorption capacity. RSCC is capable of removing phenol from an aqueous solution to the extent of 96% at the solution pH. The adsorption process obeys Freundlich adsorption isotherm. The values of adsorption capacity (k) and intensity of adsorption (n) indicate the greater affinity for phenol by this carbon. The kinetics of adsorption of phenol by RSCC follow first order reversible kinetics. The low value of k_2 (desorption process) indicates that the adsorbed phenol remains almost stable on the adsorbent and can be recovered from the adsorbent by desorption with sodium hydroxide. The regenerated adsorbent can be reactivated and reused. The results also demonstrate that an intraparticle diffusion mechanism plays a significant role in the adsorption and it is apparent that the adsorption rate is controlled by the film diffusion process. It is concluded that the activated carbon prepared from rubber seed coat could be exploited for commercial applications in the tertiary level treatment of potable water as well as industrial effluents.

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References

[1] USEPA, Industrial wastewater, Report No. EPA-600/8-80-26 (1980).
[2] J.K. Spiker, D.L. Crawford, E.C. Thiel, Appl. Microb. Biotechnol. 37 (1992) 518.
[3] K.H. Lanouette, Chem. Eng. 84 (22) (1977) 99.
[4] W.M. Throop, J. Hazard Mater. 1 (1977) 319.
[5] J.A. Klein, D.D. Lee, Biotechnol. Bioeng. Symp. 8 (1978) 379.
[6] M. Streat, J.W. Patrick, M.J. Camporro Perez, Water Res. 29 (1995) 467.

[7] G.Q. Lu, J.C.F. Low, C.Y. Liu, A.C. Lua, Fuel 74 (1995) 344.
[8] G.Q. Lu, Environ. Prog. 15 (1996) 12.
[9] S.K. Srivastava, V.K. Gupta, N. Johri, M. Dinesh, Indian J. Chem. Technol. 2 (1995) 333.
[10] V.K. Gupta, S. Saurabh, I.S. Yadav, M. Dinesh, J. Chem. Technol. Biotechnol. 71 (1998) 180.
[11] V.K. Gupta, S.K. Srivastava, T. Renu, Water Res. 34 (2000) 1543.
[12] J. Ding, V.L. Snoeyink, R.A. Larson, M.A. Recktenwalt, C.A. Wedeking, JWPCF 59 (1987) 139.
[13] D.O. Cooney, Z. Xi, AIChE J. 40 (1994) 361.
[14] T.M. Grant, C.J. King, Ind. Eng. Chem. Res. 29 (1990) 264.
[15] J.W. Hassler, Purification with Activated Carbon, Chemical Publishing Co. Inc., New York, 1974.
[16] R.U. Edgelhill, G.Q. Lu, J. Chem. Technol. Biotechnol. 71 (1998) 27.
[17] A.A.M. Daifullah, B.S. Girgis, Water Res. 32 (1998) 1169.
[18] S. Rengaraj, B. Arabindoo, V. Murugesan, Indian J. Environ. Health 41 (1999) 16.
[19] S. Rengaraj, R. Sivabalan, B. Arabindoo, V. Murugesan, Indian J. Chem. Technol. 7 (2000) 127.
[20] S. Rengaraj, Seung-Hyeon Moon, R. Sivabalan, Banumathi Arabindoo, V. Murugesan, Waste Manage., 2001, in press.
[21] S. Rengaraj, B. Arabindoo, V. Murugesan, J. Sci. Ind. Res. 57 (1998) 129.
[22] S. Rengaraj, B. Arabindoo, V. Murugesan, Indian J. Chem. Technol. 6 (1999) 1.
[23] APHA, Standard Methods for the Examination of Water and Wastewater, 17th Edition, American Water Works Association, New York, 1989.
[24] ISI, Activated Carbon, Powdered and Granular-Methods of Sampling and Tests, Bureau of Indian Standards, New Delhi, IS 877, 1989.
[25] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd Edition, ELBS, London, 1969.
[26] A.K. Battacharya, C. Venkobachar, ASCE Proc. 110 (1984) 110.
[27] C. Namasivayam, K. Renganathan, Water Res. 29 (1995) 1737.
[28] S.Ed. Gladstone, A Text Book of Physical Chemistry, Macmillan, Little Essex Street, London, 1946.
[29] G. McKay, H.S. Blair, J.R. Garden, J. Appl. Polym Sci. 27 (1982) 3043.
[30] K. Srinivasan, N. Balasubramanian, T.V. Ramakrishna, Indian J. Environ. Health 30 (1988) 376.
[31] L.D. Michelson, P.G. Gideon, E.G. Pace, L.H. Kutal, Removal of Soluble Mercury from Wastewater by Complexing Techniques, US Department of Industry, Office of Water Research and Technology, Bulletin No. 74, 1975.