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Research Article

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Removal of salicylic acid by adsorption on activated carbon: A kinetic study

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ABSTRACT

A commercially available activated carbon has been tested as an adsorbent for the removal of salicylic acid from aqueous solutions. The effect of system variables such as pH of the solution, contact time, adsorbent dosage, solute concentration and temperature has been studied. The percentage removal of salicylic acid is found to increase with an increase in salicylic acid concentration. The amount of salicylic acid adsorbed decreases when the pH increased from 4.0 to 8.5. Kinetics of removal is found to follow the first order rate expression. The adsorption data fitted into the Langmuir isotherm equation in the whole range of concentrations studied.

Keywords: Adsorption, Salicylic acid, Activated Carbon, Kinetic Study.

INTRODUCTION

The contamination of ground water is mainly due to indiscriminate disposal of wastes from various industries. A large amount of wastewater is generated by textile processing, pulp and paper making, oil refineries, fertilizers, pesticide, insecticide, detergent, food, pharmaceutics and comsmetic industries. The important organic contaminants in industrial wastewater include a variety of organic compounds such as dyes, phenols, chlorophenols, alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, polymers and surfactants. Among the carboxylic acids, salicylic acid has been identified as a water pollutant which arises from a number of sources including paper milling, cosmetic industries and as land fill leachate¹. Salicylic acid is used in wart - removing medicines,to treat fungus infections, as an acne topic treatment and to increase the cell turnover as a component of skin creams. Salicylic acid is also used as an intermediate in the manufacture of dyes. The removal of salicylic acid in water is of considerable interest. Adsorption has attracted attention in advanced water treatment methods. It has gained prominence as a treatment process for effluents that are low in the concentration of dissolved organic compounds. Adsorption technique has been widely used for the removal of various organic compounds^{2,3,4}. A variety of adsorbents such as activated carbon, silica, alumina, bentonite, peat, chitosan and ion-exchange resins have been used for the removal of organic compounds from aqueous solutions^{5,6}. Activated carbon is one of the oldest and most widely used adsorbent for the adsorption of organic compounds. It has been used in powder or granular form. The investigation reported here deals with the adsorption studies on granular activated carbon for the removal of salicylic acid at different temperatures and pH. The adsorption dynamics has been evaluated.

EXPERIMENTAL SECTION

A commercially available activated carbon with mesh size 8×32 was used as such for adsorption studies. Salicylic acid and other chemicals used in the present study were of reagent grade obtained from Merck and CDH. The solutions were prepared using double distilled water. The BET (Brunauer- Emmett- Teller) surface area of activated carbon was determined by flow method using Micromeritics pulse chemisorb 2700. The surface area of activated carbon was found to be 400 m²/g. Batch experiments were carried out by taking known amount of activated carbon with a 100 ml of salicylic acid solution in a conical flask. The solutions after adjusting pH were equilibrated for 60 minutes in a temperature controlled shaking incubator. The agitation speed, *p*H and temperature were maintained at 90 rpm, 7.0 ± 0.1 and 30.0 ± 0.1 °C respectively throughout the experiments, except where otherwise specified. The samples of 3 ml were

withdrawn at regular intervals of time and centrifuged. Absorbance of the supernatant solution was measured and returned to the reactor. The quantitative estimation of the salicylic acid was carried out using a Systronics single beam, UV – visible spectrophotometer, model – 118 at λ_{max} of 300 nm.

RESULTS AND DISCUSSION

Effect of initial concentration and contact time

The effect of initial concentration and contact time on the removal of salicylic acid was studied. Rapid uptake of organics was observed during the initial stage of contact and 50 % removal was observed within first 20 minutes and equilibrium time was around 60 minutes. A series of experiments were undertaken for varying initial salicylic acid concentration ranging from 13.8 to 22.1 mg/L. The removal of salicylic acid was found to increase from 1.28 to 1.83 mg/g by increasing the concentration from 13.8 to 22.1 mg/L at temperature 30 °C and *p*H 7.0 as shown in Fig.1. This shows that the removal of salicylic acid is highly concentration dependent. The removal curves were found to be smooth and continuous indicating the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent⁷.



Figure 1 Effect of concentration on the adsorption of salicylic acid Adsorbent dose = 5.0 g/L; $pH=7.0 \pm 0.1$; Temperature = $30^{\circ}C$; Absorbance measured at 300nm; Agitation speed = 90rpm



Figure 2 Effect of pH on the adsorption of salicylic acid [Salicylic acid] = 13.8 mg/L;Temperature = 30°C; Adsorbent dose = 5.0 g/L; Absorbance measured at 300nm; Agitation speed = 90rpm

Effect of pH

The effect of *p*H on the adsorption of salicylic acid was studied in the range of 4.0 to 8.5. The amount salicylic acid adsorbed from the aqueous solution decreased from 1.56 to 1.27 mg/g when the *p*H increased from 4.0 to 8.5 (Fig.2). The similar results were reported by Ford⁸. The removal efficiency was found to be 57 % at *p*H 4.0 and decreases to 46 % at *p*H 8.5. This may be due to the neutralization of negative charges at the surface of the carbon with increasing hydrogen ion concentration, thereby reducing hindrance to diffusion and making available more of the active surface of carbon⁹.

Effect of adsorbent dose

The effect of adsorbent dose on the removal of salicylic acid was studied in the range of 2.5 to 7.5 g/L at 30 °C and pH 7.0. It was observed that the amount of salicylic acid removal increases with an increase in adsorbent dose. The percentage removal of salicylic acid varies linearly with increase in the weight of the activated carbon. It was observed that the percentage removal of salicylic acid increases from 25 to 67 at 60 minutes of contact time , on increasing the adsorbent dose from 2.5 to 7.5 g/L on an initial concentration of 13.8 mg/L.as shown in Fig. 3.



Figure 3 Effect of adsorbent dose on the percentage removal of salicylic acid [Salicylic acid] = 13.8 mg/L; pH= 7.0 ± 0.1; Temperature = 30°C; Adsorbent = Activated carbon; Absorbance measured at 300nm; Agitation speed = 90rpm

Adsorption dynamics

The overall rate constant for adsorption $(k_{ad} \text{ min}^{-1})$ of the salicylic acid was evaluated in the light of Lagergren rate equation¹⁰ as given in Eq. 1.

$$\log\left(q_e - q_l\right) == \log q_e - \frac{k_{ad}}{2.303} \tag{1}$$

Where q_t and q_e are the amounts of salicylic acid adsorbed in mg by 1g of activated carbon at time 't' (min) and at equilibrium respectively. Lagergren plot for salicylic acid for an initial concentration of 13.8 mg/L at 30 °C and at pH 7.0 is shown in Fig. 4. The straight line plot of log $(q_e - q_t)$ verses time shows the validity of Lagergren equation and suggests that the removal of salicylic acid obeys first order kinetics. The k_{ad} values obtained for various concentrations of salicylic acid was found to be constant and lie in the range of $0.04 \pm 0.004 \text{ min}^{-1}$.

Effect of temperature

The effect of temperature was studied in the range of 30 to 50 °C. The k_{ad} values obtained for various temperatures did not show significant decrease and it remains almost constant. The values lie in the range of 0.04 ± 0.004 min⁻¹. This indicates that the effect of temperature on the adsorption of salicylic acid is negligible and suggests that the adsorption process is exothermic reaction¹¹.



Figure 4 Lagergren plot for the adsorption of salicylic acid [Salicylic acid] = 13.8 mg/L; pH= 7.0 ± 0.1; Temperature = 30°C; Adsorbent dose = 5.0g/L; Absorbance measured at 300nm; Agitation speed = 90 rpm

Adsorption isotherm

Adsorption equilibrium data expresses the relationship between the mass of adsorbate per unit weight of the adsorbent and liquid phase equilibrium concentration of adsorbate. The equilibrium data for the removal of salicylic acid in the present investigation was analysed using Freundlich and Langmuir isotherms. The linear form of the rearranged Langmuir isotherm model is represented as follows (Eq. 2).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$
(2)

Where C_e is the concentration of solute remaining in the solution at equilibrium. Q_0 and b are Langmuir isotherm constants. The linear plot of C_e versus C_e / q_e yielded a straight line showing the applicability of Langmuir isotherm as shown in Fig. 5. The values of Langmuir constants calculated are given in Table 1. From the experimental data the decrease in the value of 'b' with an increase in temperature from 30 to 50 °C indicates that the reaction is exothermic.

Table 1.Langmuir constants for the adsorption of salicylic acid

Temperature	Langmuir constants		Coefficient of correlation
(⁰ C)	Q ₀ mg/g	b L/mg	Coefficient of correlation
30	4.2	0.060	0.94
40	4.3	0.058	0.94
50	4.4	0.054	0.94

The equilibrium parameter R_L is represented as follows (Eq. 3).

$$R_{L=} \frac{1}{1+bC_0} \tag{3}$$

Where b is the Langmuir constant and C_0 is the initial concentration of salicylic acid. The R_L value of 0.55 obtained for the initial concentration of 13.8 mg/L at 30 0 C is in the range of 0>R_L<1 and shows that adsorption is favourable. The Freundlich adsorption is otherm is given by the expression (Eq. 4).

$$\log q_e = \log K + \frac{1}{n} \log C_e \tag{4}$$

The adsorption data did not fit into the Freundlich adsorption isotherm.



Figure 5 Langmuir adsorption isotherm for the adsorption of salicylic acid $pH=7.0 \pm 0.1$; Adsorbent dose = 5.0 g/L; Absorbance measured at 300nm; Agitation speed = 90rpm

CONCLUSION

The experimental results show that activated carbon is suitable for the removal of salicylic acid. The amount of salicylic acid adsorbed decreases when the pH increased from 4.0 to 8.5. The extent of removal increases with an increase in adsorbent dose. The adsorption efficiency increases with increase in salicylic acid concentration employed in the study. Kinetics of removal was found to follow the first order rate expression. The adsorption data fitted into the Langmuir isotherm equation in the whole range of concentrations studied. The effect of temperature is insignificant in the adsorption process.

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