



## USE OF POLYVINYL ALCOHOL COATED CARBON BLACK FOR REMOVAL OF LINEAR ALKYL BENZENE SULPHONATE (LAS) FROM WASTEWATERS

**Kailash Daga and Poonam Gehlot**

Enviro-Industrial Laboratory, Department of Chemistry, M. B. M. Engineering College  
Jai Narayan Vyas University, Jodhpur-342 001, Rajasthan

### ABSTRACT

The aim of the work is to study the adsorption of surfactants onto adsorbents in a batch adsorber. A comparative evaluation of the low cost and biodegradable naturally occurring adsorbents of plant origin as potential adsorbent is made against poly vinyl alcohol coated charcoal for removal of surfactants from aqueous solution. Batch kinetic and isotherm experiments were conducted to determine the adsorptive behaviour of the surfactant from aqueous solution.

### INTRODUCTION

Textile finishing industry wastewaters contain high concentration of surfactants. Surfactants derived from detergent products are the most abundant synthetic organic substances in sewage biosolids and concentration ranging from 200-2000 mg/kg dry wt. has been reported (Haig 1996). The objective of the work is to develop a better method for the removal of surfactants using low cost adsorbent. Investigations have been undertaken to evaluate low cost alternative materials as potential adsorbents for surfactants using activated carbon as reference. The alternatives considered included Fuller's earth, furnace black, activated alumina and activated sludge etc. Activated carbon adsorption has been extensively studied as a wastewater treatment method for removal of surfactants from wastewater. Carbon adsorption of surfactants is neither efficient nor economical when used alone, but when used in addition with certain polymers, it becomes a very useful polishing step for efficient surfactant removal. In the paper, a comparative study to explore the potential of activated wood charcoal (AWC) and polyvinyl alcohol coated carbon black (PVA-WC) to treat artificially made surfactant water has been conducted, and effects of pH, contact time, concentration and temperature on the adsorption were evaluated. Equilibrium adsorption capacity was studied using Langmuir and Freundlich isotherms. The adsorption of linear alkylbenzene sulphonate on both AWC and PVA-WC was found to confirm the two isotherms.

This paper deals with the preparation and adsorption capacities of activated carbon prepared from leaves of *Calotropis procera*, a desert plant and polyvinyl alcohol coated carbon black prepared from furnace black.

### MATERIALS AND METHODS

**Preparation of activated carbon from *Calotropis procera* (AWC):** Natural substances of base materials like wood are first subjected to heating process known as carbonization in which fixed carbon is formed, which is then activated by heat-stream treatment (200-1600°C). It is activated by washing with phosphoric acid and zinc chloride etc. It was cut into small pieces. The wood was treated with concentrated sulphuric acid (five times its volume) and kept in oven at 150°C for

24 hours. It was filtered and washed with distilled water repeatedly to remove sulphuric acid (washing tested with two drops of barium chloride solution) and finally dried. The adsorbent is sieved to 40-60-mesh size and heated at 150°C for 2 hours. This material is used as an adsorbent to study adsorption of the surfactant at different pH. This adsorbent was also added to polyvinyl alcohol coated carbon black to form a new adsorbent having a fine particle size for removing the surfactant.

**Polyvinyl alcohol coated carbon black (PVA-WC):** Polyvinyl alcohol is a good hydrophilic polymer and has water-adsorbing capacity. The carbon black used for adsorption is furnace black. The furnace black is obtained from the burning of furnace oil in absence of sufficient oxygen at higher temperature. This carbon black (commonly named furnace black) is in the form of very fine particles.

**Preparation of polyvinyl coated carbon black:** One gramme of PVA is dissolved in 90 mL hot water to form a gel. 1, 1.5, 2 and 2.5 g of furnace black is added in it to form a thick paste. This paste was then mixed with activated carbon obtained from the wood of *Calotropis procera*. The thick paste obtained was then dried to form lumps. The lumps were grinded into fine powder. This powder was used as an adsorbing material. The four samples of PVA coated activated wood charcoal + furnace black were prepared as follows:

Adsorbent	PVA	Furnace Black	Activated Wood Charcoal
I	1 g	1.0 g	10 g
II	1 g	1.5 g	10 g
III	1 g	2.0 g	10 g
IV	1 g	2.5 g	10 g

### Batch Experiment

To study the adsorption capacities of these adsorbents, batch experiments were carried out. The variables studied were contact time, initial surfactant concentration, pH and adsorbent dose. The adsorbent dose varied from 1.0 to 2.5 g. During experiment, the system was continuously stirred and at the end of each experiment the solution was centrifuged and filtered through Whatman filter paper. The surfactant concentration in the wastewater before and after the batch experiment was studied spectrophotometrically in visible region.

### Adsorption Studies

The changes in pH of aqueous phase cause significant changes in the anionic surfactant adsorption at the charged adsorbent surface. In the adsorption measurement LAS solutions at different concentrations (20 to 80 ppm) and pH (3, 5, 8 and 10) were used. HCl and NaOH adjusted the pH of the solutions. Various doses of adsorbent were added to surfactant solution prepared at different pH and concentrations. The equilibrium adsorption of LAS was reached in 120 min. The solutions were stirred at constant speed. After 120 min, the concentration of LAS in solution was measured by an UV-VIS spectrophotometer.

The percentage of adsorbed surfactant (PAS) was calculated by the following equation.

$$PAS = [(C_o - C_e)/C_o] \times 100 \quad \dots(1)$$

$C_o$  is initial surfactant concentration in solution and  $C_e$  is equilibrium surfactant concentration in solution. The concentrations of surfactants and pH values of LAS were measured by UV-VIS spectrophotometer between 15 and 180 min.

Table 1: Kinetic constants for adsorption of the surfactant at 30°C.

Adsorbent	$K_{id}$	$K_{ad}$
AWC	0.8493	0.0303
PVA-WC	0.9041	0.0384

For the effect of pH on the adsorption of LAS, adsorption isotherms of the surfactant and adsorption kinetics were investigated. With the decreasing values of pH and surfactant concentration, adsorption rate and the amount of surfactant adsorbed by the adsorbent increase. At pH 3, 20 ppm of LAS was adsorbed by adsorbent PVA coated wood charcoal and AWC at the percentage of 59.4 and 54.6 respectively.

The rate constant for intra-particle diffusion is given by the expression:

$$K_{id} = q/t^{1/2} \quad \dots(2)$$

Where q is the amount adsorbed (mg/g) at time t (min) and  $k_{id}$  is intra-particle rate constant

$$Q_e = K_f C_e^{1/n} \quad \dots(3)$$

$$\log (q_e - q) = \log q_e - K_{ad} T/2.303 \quad \dots(4)$$

The values of  $K_{id}$  and  $K_{ad}$  are given in Table 1. The results of the study are graphically presented in Figs. 1, 2, 3 and 4.

**Principle of Adsorption Isotherms**

Adsorption efficiency is tested by adsorption isotherms. Two isotherms are frequently studied for adsorption process, Freundlich and Langmuir isotherms.

The relation between the surfactant (LAS) adsorbed by the different adsorbents and surfactant equilibrium concentration in solution is given by Freundlich adsorption isotherm.

The Freundlich equation is used for heterogeneous surface energies in which the energy term,  $Q_o$  in the Langmuir equation varies as a function of the surface coverage and  $q_e$  is strictly due to variations in the heat of adsorption.

$$q_e = k_f C_e^{1/n} \quad \dots(5)$$

The linear form of the equation (1) or the log form is:

$$\log q_e = \log k_f + 1/n \log C_e \quad \dots(6)$$

Where  $C_e$  is the equilibrium concentration (mg/L) and  $q_e$  is the amount adsorbed (mg/g) at equilibrium time; and  $k_f$  and n are Freundlich constants. n gives an indication of the favourability and  $k_f$  the capacity of the adsorbent. Value of n between 1 and 10 indicates good adsorption.

Langmuir isotherm governs the monolayer coverage of the surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbents in the plane of surface. The Langmuir isotherm is represented by the following equation:

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad \dots(7)$$

Where,  $C_e$  is equilibrium concentration (mg/L), q is the amount at equilibrium time per unit

Table 2: Langmuir and Freundlich constants for adsorption of LAS on PVA-WC and AWC at 120 min and at optimum dose of 1 g/L.

	Langmuir				Freundlich			
	Q <sup>o</sup> (mg/g)	b(L/mg)	r	r <sup>2</sup>	K <sub>f</sub>	n	r	r <sup>2</sup>
PVA-WC	35.21	0.0424	0.9940	0.9881	3.12	1.89	0.9736	0.9480
AWC	64.51	0.0160	0.9950	0.9902	1.69	1.36	0.9957	0.9916

r: Correlation coefficient    r<sup>2</sup>: Coefficient of determination

Table 3: Data of Langmuir and Freundlich adsorption isotherms for adsorption of LAS (PVA-WC).

Adsorbent dose (g/L)	Langmuir isotherm (Linear equation)	Freundlich isotherm (Linear equation)
1 g/L	Y = 0.0284x + 0.6689	Y = 0.5291x + 0.4950
1.5 g/L	Y = 0.0362x + 0.7910	Y = 0.5346x + 0.3989
2.0 g/L	Y = 0.0413x + 0.6952	Y = 0.4967x + 0.4461
2.5 g/L	Y = 0.0426x + 0.7023	Y = 0.5185x + 0.4108

adsorbent (mg/g), and Q and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter  $R_L$  which is defined by:

$$R_L = 1/(1+bC_o) \quad \dots(8)$$

Where,  $C_o$  is the initial adsorbate concentration (mg/L) and b is the Langmuir constant (mg/L).

### Adsorption Rate Constants

The overall rate constant for adsorption ( $k_{ad}$ , l/min) of an adsorbate is given by Lagergren,

$$\log (q_e - q) = \log q_e - k_{ad} T/2.303 \quad \dots(9)$$

Where, q and  $q_e$  are the amounts of adsorbate adsorbed (mg/g) at time t (min) and equilibrium respectively.

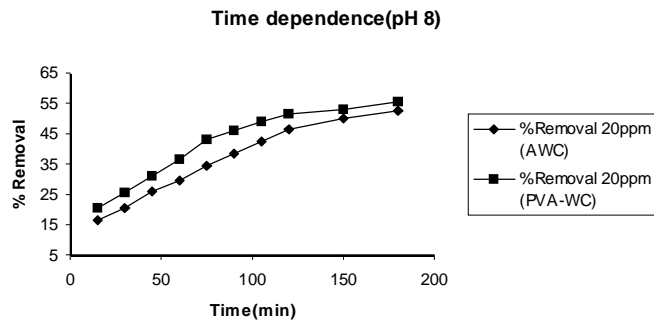


Fig. 1: Effect of contact time on adsorption of different concentration of LAS on AWC and PVA-WC at pH 8.

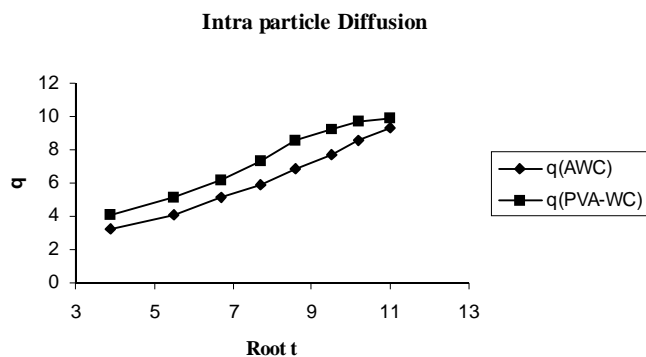


Fig. 2: Relation between the amount adsorbed ( $q$  mg/g) and the square root of the time (AWC and PVA-WC).

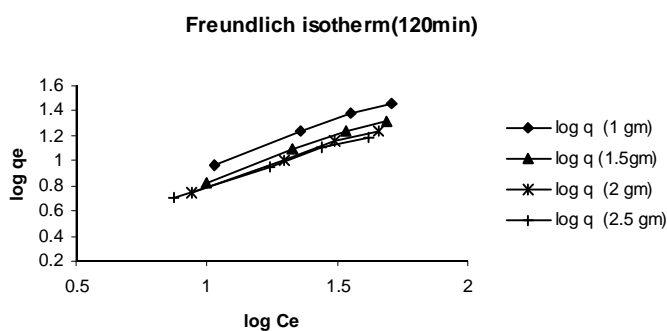


Fig. 3: Freundlich isotherm for effect of different adsorbent amounts on adsorption of LAS on AWC at different concentrations at constant contact time of 120 minutes.

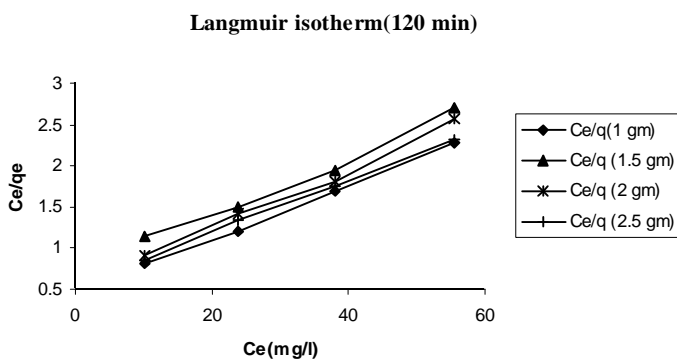


Fig. 4: Langmuir isotherm for effect of different adsorbent amounts on adsorption of LAS on PVA-WC at different concentrations at constant contact time of 120 minutes

The correlation coefficient ( $r$ ) and coefficient of determination ( $r^2$ ) for Freundlich and Langmuir isotherms are merely equal. Therefore, for the present adsorption study, it can be stated that Freundlich and Langmuir adsorption equations are found to be better fitted. The data on the Langmuir and Freundlich constants and adsorption isotherms are given in Tables 2 and 3.

The effect of isotherm on whether adsorption is favourable or unfavourable has been considered. Values of dimensionless equilibrium parameter  $R_L$  show the adsorption to be favourable ( $0 < R_L < 1$ ).

### **CONCLUSION**

According to the results, it can be concluded that PVA coated wood charcoal adsorbent is more effective in the removal of surfactant, LAS, at low pH values and concentrations. The adsorbed amount of LAS on PVA coated wood charcoal as adsorbent and its adsorption rate are higher than for LAS adsorption on AWC as adsorbent

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