Performance of Carbonized Agricultural Waste as a Low-Cost Adsorbent for the Removal of Sodium Dodecyl Sulfate from Aquatic Environment

Manisha A. Agrawal, Jyoti Kapil Nagwanshi, Sangeeta Patil

Abstract— Removal of higher concentration of sodium dodecyl sulphate from waste water, using carbonized orange peel as an adsorbent has been discussed in the present investigation. Carbonized orange peel charcoal has been prepared in the lab by using muffle furnace at high temperature. Efficiency of removal of SDS is measured by pH meter using batch technique. Various concentration of SDS solutions from 1×10^{-4} to 12×10^{-4} M have been prepared and their pH values assessed before and after adsorption on carbonized peel. By using the data, result shows a straight line pattern. Various adsorption Isotherms like Langmuir adsorption Isotherms, Freundlich adsorption Isotherms and Temkin adsorption Isotherms are discussed and compared.

Index Terms— Adsorption Isotherms, Sodium Dodecyl Sulphate, Surfactant, Carbonization, Adsorption, Freundlich Adsorption Isotherms, Temkin Adsorption Isotherms.

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1 INTRODUCTION

AS a consequence of water problem it would be judicious for any rational water management authority to secure the purest water sources for direct human consumption and to encourage the reuse of processed water for industrial applications. Environmental risks associated with detergent manufacture, its use and disposal are of great concern due to the relative toxicity of detergent products and its core ingredient surfactants on aquatic life. Surfactants are found in a wide variety of commercial products such as industrial and household detergents, emulsifiers, adhesives, and paints. It is found in toothpaste, shampoo, shaving cream and bubble bath formulations in part for its thickening effect and its ability to create lather [1].

The role of surfactants in the environment is ambiguous. They can cause serious environmental pollution with increased toxicity in living organisms; whilst on the other hand; they can promote removal of inorganic and organic pollutants from the environment. Due to the diversity of surfactants and their physico-chemical properties, it is difficult to develop a single and an effective treatment method of detergent wastewater.

Some techniques or methods which are useful for removal of surfactants are listed as biodegradation, coagulation, foaming, adsorption, ion-exchange, membrane filtration, and UV irradiation [2-4]. Among all process adsorption process re-

ceived much more attention. For the adsorption purpose, charcoal is an effective material because of its high surface area. Adsorption using activated carbon is most widely used method to remove organic as well as inorganic materials from waste water, because of its low cost, ease of operation and good result. But its use is limited because of high cost and associated problem of regeneration, there is a constant search for cheaper substitutes. Many efforts have been made to use low cost agro waste materials studied for their capacity to remove heavy metals [5] organic dyes [6,7] from waste water . But removal of surfactant from water is still a thrust area.

In the present investigation we have taken a non-conventional, eco friendly, bio-degradable agro-waste material - orange peel for adsorption of surfactant.

2 EXPERIMENTAL PROCEDURE

2.1 Sample collection

The orange peel was collected on the month of December, January. The peels were sun dried, and then oven dried at $100°C$ until properly dried. The peel was grounded and sieved with a 2 mm mesh size sieve. The less than 2 mm samples were used for the preparation of carbonized orange peel.

2.2 Preparation of adsorbent from agro-waste

5g of blended dried orange peel was weighted into clean and pre weight crucibles. They were introduced into a muffle furnace at $600°C$ for 4 minutes. After that red hot carbonized char were poured into ice cold water. The excess water was drained out, and remaining char was washed twice with distilled water .The char was then sun dried, and further dried in the oven at $100 - 110°C$ overnight and stored in air tight container [8,9].

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2.3 Reagent preparation

All chemicals used are of analytical grade. Double distilled water had been used for the preparation of solutions sodium dodecyl sulfate (SDS, C12H25SO4Na). Aqueous solutions of SDS having initial concentrations Ci equals 1×10^{-4}, 2×10^{-4}, 3×10^{-4}, 4×10^{-4}, 5×10^{-4}, 6×10^{-4}, 7×10^{-4}, 8×10^{-4}, 9×10^{-4}, 10×10^{-4}, 11×10^{-4} and 12×10^{-4} M were prepared .The pH values of each solution was determined using digital pH meter before and after adsorption [10] . The carbonized, orange peel charcoal (OPC) used as adsorbent is up to 2.0 mm. The determination of adsorption of (SDS) from each solution on OPC was carried out using batch technique by adding 1.0 gram OPC to 100 ml. of each solution in 250 ml conical flask, with shaking for 45 minutes using electric shaker for the same time and speed, then each solution was filtered through filter paper without washing the remainder OPC.

3 RESULTS AND DISCUSSION

The salt Sodium dodecyl sulphate (SDS) is an organo-sulphate compound consisting of a 12 carbon chain attached to a sulphate group, which gives amphiphilic nature. These properties are essential for detergent. The mechanism and adsorption isotherm of adsorption of SDS on OPC can be studied by measuring change in the pH values of the SDS solutions before and after adsorption for different initial concentrations Ci. Line A and line B in Fig. 1 shows the change in the pH values of different initial concentration solutions before and after adsorption through OPC, respectively. Values indicate that, an increase in initial concentration Ci means increase of pH val-

Fig. 1: Represents the change of pH of SDS solutions with its Concentration C_i ML^{-1}
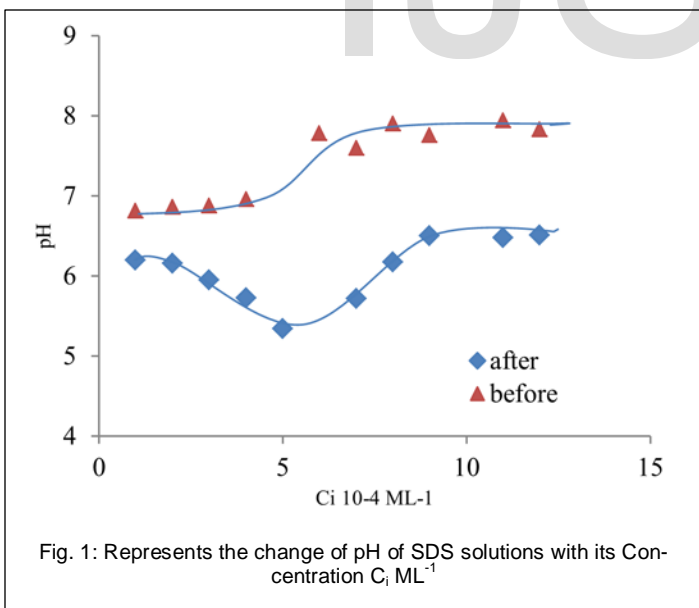
ue. This trend obtained in both lines, which is having good agreement as the result obtained by Ismaeel [10].

As per absorption mechanism one mole OH- will release after absorption of one mole of SDS. So equilibrium concentration can be calculated according to the number of moles of SDS absorbed.

The adsorption behavior of SDS on OPC can be explained by using Helmholtz plane, The hydrated negative Sodium dodecyl sulphate anion move with its negative sulphate end facing to carbon surface due to electrostatic attraction with partial positive charge on the hydrogen of the molecules of primary water layer adsorbed on OPC surface at the Helmholtz plane of the solution – charcoal double layer, the adsorption mechanism is illustrated by the following Eq. (1):

$$CH_3(CH_2)_{11}O - SO_3^- + H_2O \rightarrow CH_3(CH_2)_{11}O - SO_3 H + OH^-$$
(1)
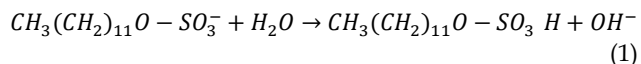
From this mechanism one mole SDS absorbed on Helmholtz O plane releasing one mole of hydroxyl anion to the positive sodium cation adsorbed in the outer Helmholtz plane of the solution-charcoal double layer to pass to solution bulk increases its pH value . This mechanism is of the postulated vertical adsorption of neutral -SO3H ion that is more possible than repulsive negative SO3- ion. Thus the liberated hydroxyl anion increases the pH value of solution after adsorption, where one mole of dodecyl sulphate is equivalent to an increase of one mole hydroxyl ion as indicated by equation (1). So we can determine the lowering of concentration Ce of SDS which is equal to $(C_i – C_f)$ to be equal to the increase of OH^- ion concentration calculated from the observed increase of pH values of solution due to adsorbtion [11].

3.1 Adsorption of SDS

Adsorption of no. of moles of surfactant (SDS) by per one gram OPC is given by the formula shown in Eq.(2):

$$x = C_e . V . Eq / 1000$$
(2)

where, x = No. of moles of SDS, V = Volume of test solution in ml, Eq= Equivalent weight of SDS in gm.

3.2 Adsorption Equilibrium

Adsorption will continue until equilibrium will be established between the substance in solution and the same substance in the adsorbed state. At equilibrium a relationship exists between the concentration of the SDS in solution and the concentration of the same species in the adsorbed state (i.e., the amount of species adsorbed per unit mass of adsorbent). The adsorption equilibrium relationship at a given temperature is typically referred to as adsorption isotherm as given in Eq.(3):

$$q = f (C_e)$$
(3)

where q = mass of SDS adsorbed. C_e = equilibrium concentration of adsorbable species in solution.

3.3 Adsorption Isotherms

Adsorption isotherms is basically important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents. An expression representing the variation of the amount adsorbed with the equilibrium concentration at a fixed temperature is known as adsorption isotherms.

If it is assumed that the uptake of SDS by the adsorbent is the result of physical adsorption or Chemical adsorption between the SDS and chemical moiety on the adsorbents then the maximum number of such sites would be finite. When the adsorbent and adsorbate come in contact with each other, dynamic equilibrium is established between the adsorbate concentrations in both the phases. The state is dynamic in nature, as the amount of adsorbate migrating onto
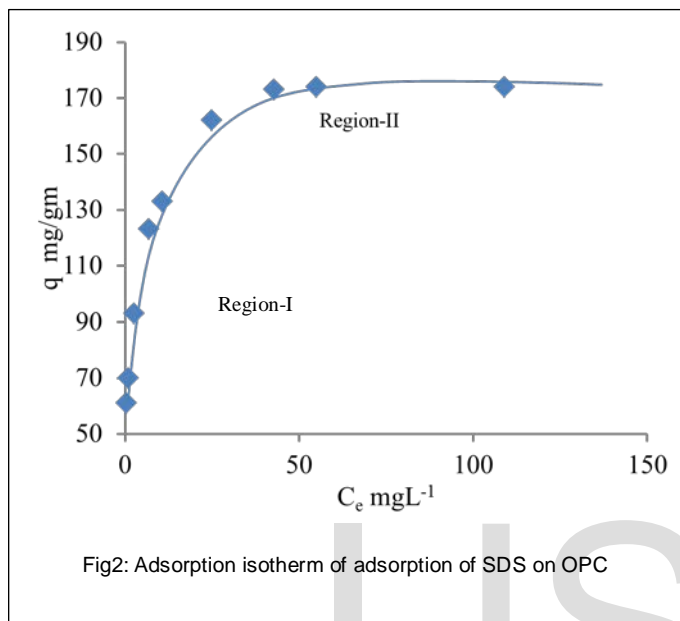

Fig2: Adsorption isotherm of adsorption of SDS on OPC

the adsorbent would be counter balanced by the amount of adsorbate migrating back into the solution. When all the sites available achieve equilibrium, the adsorptive capacity would be maximum[12].

Freundlich describe the adsorption process on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. Freundlich demonstrated that the ratio of the amount of solute adsorbed onto a given mass of an adsorbent to the concentration of the solute in the solution was not constant at different solution concentrations. The Freundlich isotherm shown in Eq. (4) assumes that

$$q = K_f C_e^{1/n} \qquad (4)$$

Where q = amount adsorbed / gm of adsorbent

Fig. 2 presents the typical isotherm of adsorption of SDS on the solid–liquid interface. Isotherm can be subdivided into three regions. In region I, the sudden rise in adsorption, in region II is due to formation of surface aggregate of the SDS molecules on the solid surface. These surface aggregates are known as 'hemimicelles' and the concentration is known as critical hemimicellar concentration (HMC). The forces causing ionic association on the solid surface will be same as those operating in the bulk. Because of the high surface charge, the dodecyl sulphate ions must necessarily be oriented with the charged head towards the surface and with tail striking out into the liquid. This type of adsorption is termed as 'head on' adsorption. Then the associative vander Waals force in the chains will be from hemimicelle. Region II shows a slower rate
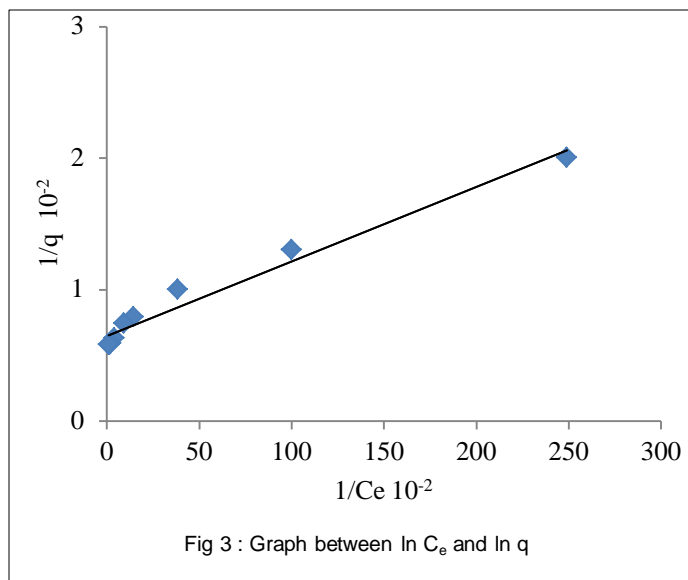

Fig 3 : Graph between ln C_e and ln q

of adsorption than region I. Region III show a maximum. Freundlich equation can be rearranged in the linear form by taking the logarithm of both sides as shown by Eq.(5):

$$log\ q\ =\ log\ K_f\ +\ 1/n\ log\ C_e \qquad (5)$$

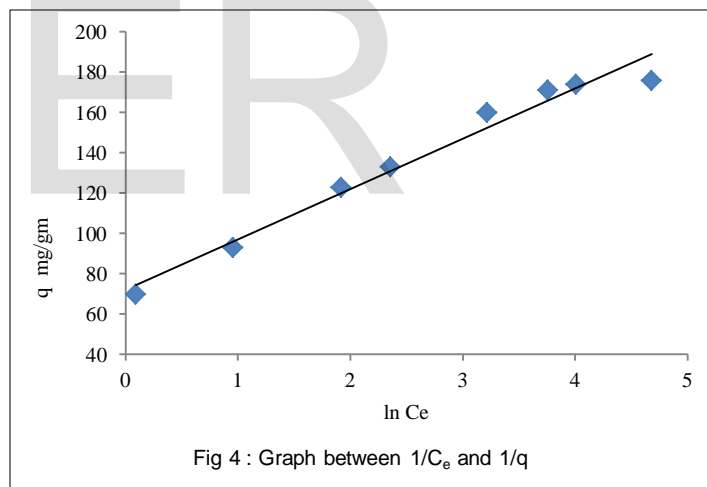Where; K_f = Freundlich equilibrium constant; C_e = equilibrium

Fig 4 : Graph between 1/C_e and 1/q

concentration, K_f is Freundlich constant related to sorption capacity. At present experimental conditions the value of K_f is 4.3 (Fig. 3). The slope 1/n is a measure for the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below one indicates a normal Freundlich / Langmuir isotherm while 1/n above one is indicative of cooperative adsorption. At present experimental conditions the value is 0.23. Hence small value shows that adsorption is good at high concentration.

In the Langmuir model adsorption is assumed to be a dynamic process. At equilibrium the number of molecules being adsorbed will be equal to the number of molecules leaving the state. To estimate maximum adsorption capacity (Q_{max}), linearized forms of Langmuir isotherms was used in Eq. (6),

$$1/q \ = \ 1/Q_{max} \ + \ 1/K_a \, Q_{max} \, (1/ \, C_e) \qquad (6)$$

where C_e is the solute concentration at equilibrium in aqueous phase in mg/L, q is the solute adsorbed per unit weight of adsorbent in mg/g. Q_{max} is the maximum solute adsorbed per unit weight of adsorbents in mg/g and K_a is Langmuir constant. Graph between $1/q$ against $1/C_e$ was drawn to get the corresponding Langmuir isotherms and from the equations obtained the maximum adsorptive capacities (Q_{max}) for the adsorbent was 1.53 mg/gm (Fig. 4).

The Langmuir constant can also used for calculation the separation factor, which predicts whether an adsorption system is favourable or unfavorable. This separation factor (r) is defined as given by Eq.(7)

$$r \ = \ 1/ \, (1 + K_a C_i) \qquad (7)$$

where K_a is Langmuir constant and C_i is the initial solute concentration. In present experimental condition the value of r ranges from 0.98 to 0.81 for the concentration 1×10^{-4} to 12×10^{-4} M. The r values for present experimental data fall between 0 and 1, which is indicative of favorable adsorption of SDS on the OPC. The r values showed that adsorption was more favorable for initial SDS concentration than for the lower one. According to the values of the correlation coefficients, R^2, it can be concluded that the Freundlich model represents the adsorption data reasonably well. Correlation coefficient is 0.9835 for Freundlich-fitting while 0.9711 for the Langmuir-fitting (Table1).

3.4 Temkin Isotherm

Linear form of Temkin isotherm [13] can be given by Eq. (8)

$$q \ = \ A \ + \ B \, ln \, C_e \qquad (8)$$

where, A = Temkin constant related to maximum binding energy. B = Temkin constant related to heat of adsorption. The plot of q versus $ln \, C_e$ gives value of A and B (Fig 5, Table 2).

Table1: Values of Langmuir and Freundlich parameters:

Correlation coefficient for Langmuir model	Correlation coefficient For Freundlich model	K_f L/gm	n	Q max mg/gm	K_a
1/q=0.0057(1/C$_e$)+ 0.6478(0.9711)	lnq=0.2297 ln C$_e$ + 4.3029(0.9835)	4.3	4.4	1.53	113

Table 2: Values of Temkin parameters

Correlation coefficient for Temkin model	A	B
q= 24.955 ln C$_e$ + 71.98 (0.9738)	71.98	24.93

4. CONCLUSION *(6)*

Adsorption of SDS on orange peel charcoal was monitored. Orange peel charcoal an unusable waste, show a relatively high adsorption capacity for surfactant. Studies proved a connection between adsorption and the change in the pH. The adsorption process can be described by investigating the adsorption isotherm, three equilibrium isotherms were analyzed: the Freundlich, the Langmuir and the Temkin isotherms. Particularly due to its adsorption capacity and price, OPC can be used as absorbing material. We can use this method in the study of adsorption of SDS in case of purification or recycling of industrial, agricultural or domestic waste water.
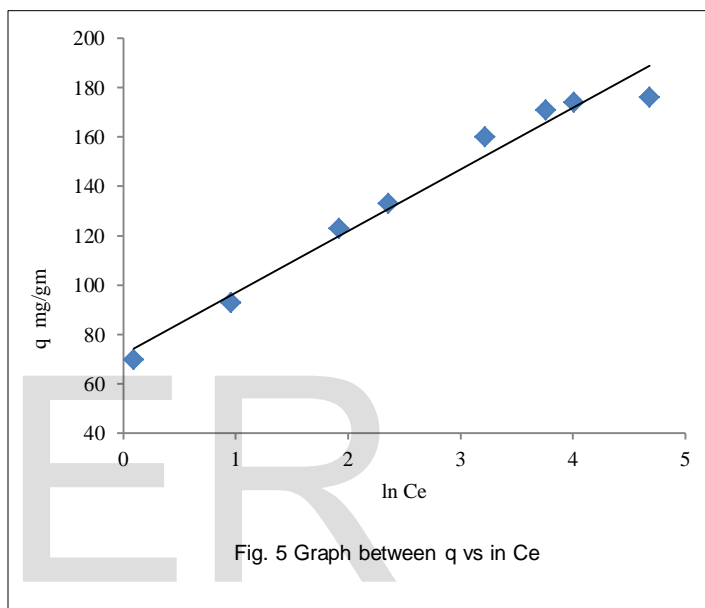

Fig. 5 Graph between q vs in Ce

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