Removal of Surfactants from Waste Water through Carbonized Charcoal of Citrus Fruits Peel

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Abstract: An eco-friendly and chemical free procedure for removing surfactant sodium do-decylsulphate (SDS), an anionic surfactant (AS) from contaminated water has been discussed in the present investigation. Experiments have performed on three different adsorbent beds of carbonized orange peel- non-activated adsorbent bed, alkali activated adsorbent bed and acid activated adsorbent bed. Efficiency of activated adsorbent bed for the removal of SDS and study of adsorption isotherms are accomplished by pH, conductivity, spectrophotometric and surface tension methods. Experiments have implemented by altering initial concentration, shaking time and adsorbent bed dosages and adsorption behavior is analyzed with Freundlich and Langmuir adsorption isotherms. Results show that the alkali activated adsorbent bed of orange peel enhances the removal efficiency of SDS from contaminated water as compared to acid activated and non-activated adsorbent bed.

Keywords: Adsorption, Adsorbent bed, Adsorption isotherm, Anionic surfactant, Sodium do-decylsulphate.

I. INTRODUCTION

The removal of surfactants from waste water is a field of research that has attracted increasing attention from the scientific community as the quest for green chemistry takes centre stage. Surfactants are used in cosmetics, soaps, detergents etc. and have detergency, wetting, emulsifying, solubilizing, dispersing and foaming effects (El-Said S. M., October 2004), (Mishra, et al., 2009). Surfactants in waste water are hazardous to the environment and therefore their removal is must. These substances are stable and persistent environmental contaminants since they are non-biodegradable. Many physicochemical methods for surfactant removal from aqueous solution have been developed. These methods include-biodegradation (Berna, et al., 2007), coagulation/flocculation (Aboulhassan, Souabi, Yaacoubi, and Baudu, 2006), foaming (Kowalska, 2008), advanced oxidation, UV irradiation (Smith and Zhou, 2002), ozonation, ion-exchange, ultra-filtration (Kowalska, 2008; Taffarel and Rubio, 2010), HPLC coupled with universal mass spectrometry detector [MS] (Olkowaska, Polkowska, and Namiesnik, 2012).

However, some of the techniques have drawbacks such as high reagent and energy requirements, insufficientsurfactant removal, a lot of time or sophisticated instruments etc. Cost effective alternative technologies to conventional methods are essential for the removal of surfactants from contaminated water. An innovative technique that is both efficient and economical is termed as adsorption (Adak, Pal, and Bandyopadhyay, 2005), (Purakayastha, Pal, and Bandyopadhyay, 2005), (Su, Zhao, Xiao, and Han, 2013). The major advantages of adsorption include low cost, high efficiency, minimization of chemical.

Orange peel is an attractive and economic alternative for the removal of surfactants from waste water. The aim of this work is to study the adsorption capacity of orange peel for removing SDS.

II. MATERIALS AND METHODS

A. Chemicals and Instruments

All the chemicals used in this study are of analytical reagent grade. SDS, cationic dye crystal violet, benzene are supplied by Merck.All the solutions have prepared in single distilled water at room temperature. Instruments used are Muffle Furnace, Digital pH Meter Model no.112, Digital Water and Soil Analysis Kit Model no. 161, Digital Spectrophotometer VSI-SPI, Traube's Stalagmometer.

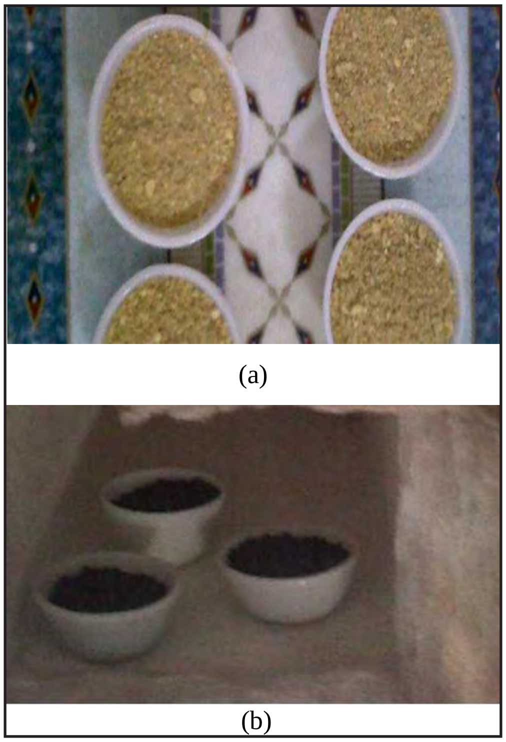
B. Experimental Procedure

1.0 gram carbonized peel along with 100.0 ml. of sample solution is shaken for 30 minutes as reported method (Agrawal, Nagwanshi, and Patil, 2013). The pH (Ismeel, Edbey, and Shagluf, 2010) and conductivity (Ali, Uzair, Malik, and Ali, 2014) of the filtrates are measured. Shook solution is transferred in a separating funnel, addition of crystal violet (CV) and orthophosphoric acid followed by further addition of 5.0 ml benzene is done (Soni, Rai, and Sar, 2012).

The contents are mixed and allowed to stand for 3 minutes. The aqueous layer is discarded and the benzene layer is used for the absorbance measurement at a wavelength of 565 nm. Blank solution is also measured in a similar manner.

C. Adsorbent Bed Preparation

The agro-waste material, orange peels used for the study arepurchased from a local market. The orange peels are washed with distilled water, dried in an oven at 80°C to constant mass and crushed into smaller particles. Crushed and grinded peels are placed in muffle furnace for carbonization (Pandharipade, Moharkar, and Thakur, 2012). Then resulting carbonized charcoal is put in air tight bottles and stored in a desiccator for further use.


(a)

(b)

Fig. 1: Orange peel (a) before carbonization (b) after carbonization

D. Adsorption Isotherm

Adsorption isotherm may be defined as - “The relationship between the amount of substance adsorbed by an adsorbent and the equilibrium concentration or equilibriumpressure at constant temperature”. Freundlichand Langmuir adsorption isotherms (Metcalf and Eddy, 2003), (AO, AP, AM, and O, 2012) are studied here to analyze the adsorption behavior.

- Freundlich adsorption isotherm is derived empirically in 1912 and may be defined as eq. (1)

$$\frac{x}{m} = K_f C_e^{1/n} \qquad \text{..... (1)}$$

where, x = quantity adsorbed (g),

m = mass of adsorbent (g),

C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/l), K_f and n = empirical constants.

- Langmuir derived empirically Langmuir Equation which depicted a relationship between the equilibrium concentration of adsorbate and mass of adsorbate adsorbed per unit mass of adsorbent. Langmuir adsorption isotherm may be defined as eq. (2)

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \qquad \text{..... (2)}$$

where, x = quantity adsorbed (g),

m = mass of adsorbent (g),

C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/l),

a and b = empirical constants.

E. Results and Discussion

The mechanism of adsorption of SDS on alkali and acid activated orange peel charcoal (OPC), its comparison with non-activated charcoal and adsorption isotherms are studied by measuring pH, conductivity, optical density (OD) and surface tension values for different initial concentrations (C_i) in Fig. 2, 3, 4 and 5. The graphs related are drawn below at room temperature 31°C, dose of adsorbent bed 1.0 g and shaking time 30 min.

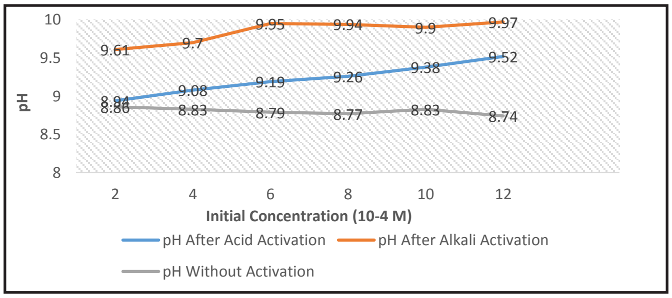


Fig. 2: A plot of Initial Concentration vs pH (non-activated, alkali and acid activated OPC)

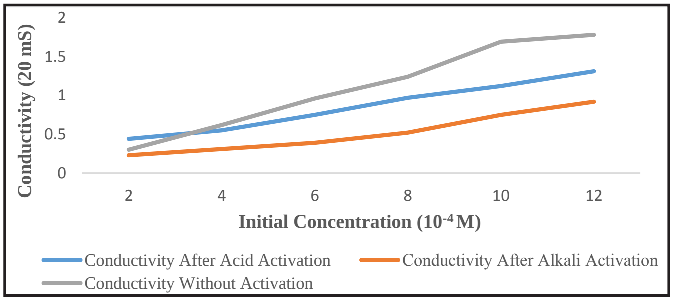


Fig. 3: A plot of Initial Concentration vs Conductivity (non-activated, alkali and acid activated OPC)

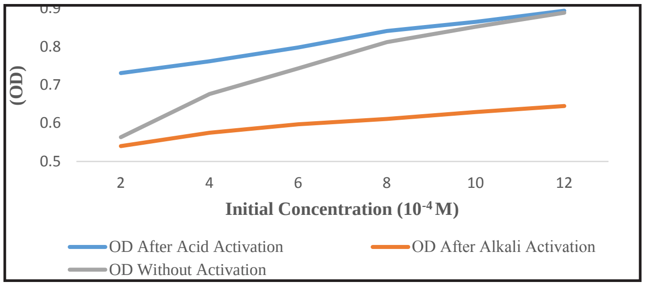


Fig. 4: A plot of Initial Concentration vs OD (non-activated, alkali and acid activated OPC)

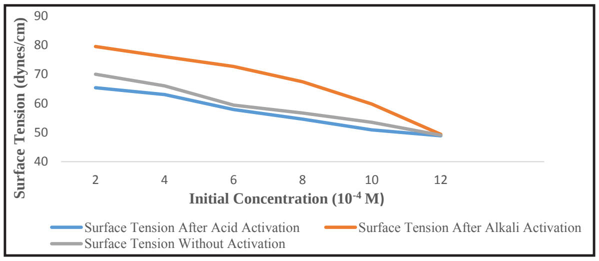


Fig. 5: A plot of Initial Concentration vs Surface Tension (non-activated, alkali and acid activated OPC)

Fig. 2, 3, 4 and 5 shows that alkali activated OPC is better adsorbent bed than acid activated or non-activated charcoal. Because after adsorption through alkali activated charcoal, greater amount of SDS gets adsorbed as it contains SO_4^{2-} ions. Thus pH of solution becomes alkaline, indicating that removal of SO_4^{2-} ions. Alkali activated charcoal adsorbs more amounts of sulfate ions from the solution and thus the values of conductivity of working solution are smaller. According to Beer-Lambert's law, smaller the value of OD, smaller will be the amount of SDS in solution. Result shows that elute obtained from alkali activated charcoal has lesser OD, thus contains smaller SDS as compared to others. As we know that larger the value of surface tension, smaller will be the amount of SDS in solution. Results show that elute obtained from alkali activated charcoal has greater surface tension, thus contains smaller SDS.

Graphs are plotted between different shaking time, pH, electrical conductance, OD and surface tension values, which are shown in Fig. 6, 7, 8 and 9 and reaction conditions are- room temperature 30.5°C, dose of adsorbent bed 1.0 g. Before adsorption, pH of the solution is 4.18 and C_i is 4×10^{-4} M.

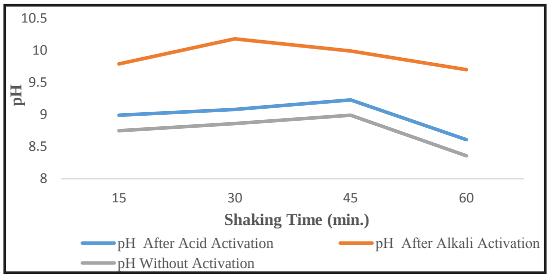


Fig. 6: A plot of Shaking Time vs pH (non-activated, alkali and acid activated OPC)

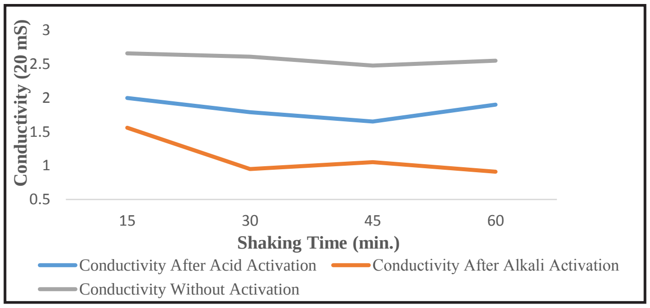


Fig. 7: A plot of Shaking Time vs Conductivity (non-activated, alkali and acid activated OPC)

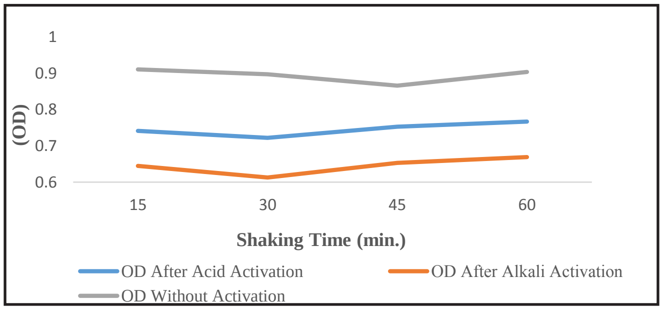


Fig. 8: A plot of Shaking Time vs OD (non-activated, alkali and acid activated OPC)

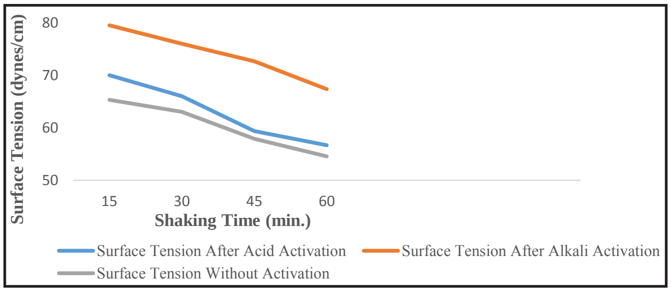


Fig. 9: A plot of Shaking Time vs Surface Tension (non-activated, alkali and acid activated OPC)

Fig. 6 shows that at 30 min. shaking time, pH after alkali activated charcoal is highest, indicating greater adsorption of SDS through this charcoal and 30 min. shaking time is sufficient for proceeding experiment. Conductivity is found least at 30 min. shaking time in Fig. 7 when passing through alkali activated charcoal, after 30 min. equilibrium reaches. Fig. 8 also indicates that alkali activated charcoal is better adsorbent bed than others. Fig. 9 shows change in surface tension at different shaking time by using alkali and acid activated charcoal and non-activated charcoal. Result shows that solution obtained from alkali activated charcoal has greater surface tension, thus contains smaller SDS.

Graphs are also plotted between different adsorbent bed dosages, pH, conductivity, OD and surface tension values in Fig. 10, 11, 12 and 13. Reaction conditions are- room temperature 31°C and shaking time 30 min. Before adsorption, pH of the solution is 4.18 and C_i is 4×10^{-4} M.

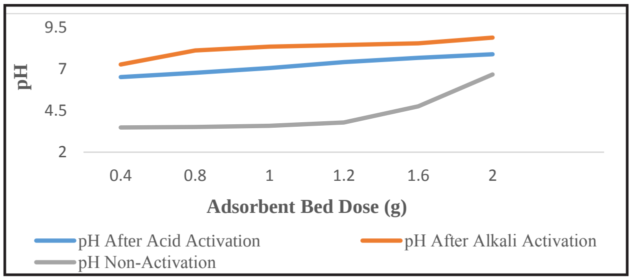


Fig. 10: A plot of Adsorbent Bed Dose vs pH (non-activated, alkali and acid activated OPC)

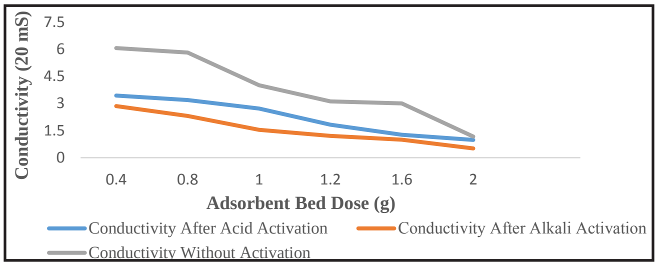


Fig. 11: A plot of Adsorbent Bed Dose vs Conductivity (non-activated, alkali and acid activated OPC)

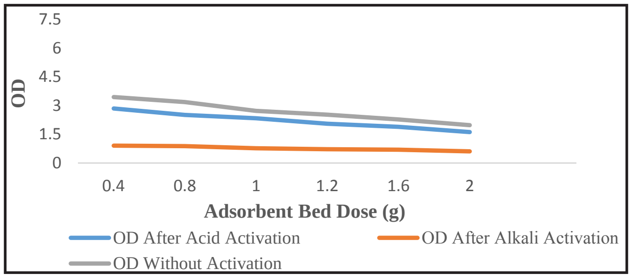


Fig. 12: A plot of Adsorbent Bed Dose vs OD (non-activated, alkali and acid activated OPC)

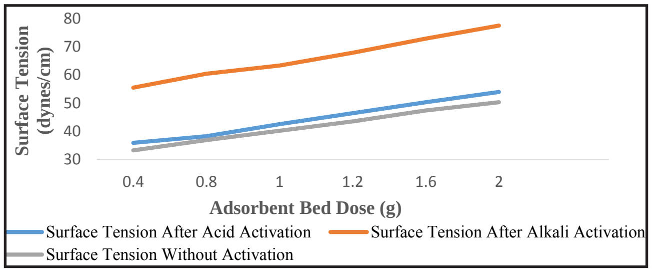


Fig. 13: A plot of Adsorbent Bed Dose vs Surface Tension (non-activated, alkali and acid activated OPC)

In all three types of beds, as adsorbent bed dose increases from 0.4 g. to 2.0 g., more and more SDS is adsorbed by adsorbent beds, number of sulphate ions becomes lesser and thus pH moves towards alkalinity. As surface area increases, adsorption process gets increased. Better result is obtained from alkali activated charcoal. In Fig. 11, initially the value of conductivity is very high, i.e. 10.01 mS, indicating the presence of larger no. of SO_4^{2-}ions in solution. As bed dosages increase from 0.4 g. to 2.0 g., conductivity decreases from 6.06 to 0.51 mS. the result displays that sufficient amount of SDS is adsorbed by 2.0 gcarbonized peel, and thus the amount of SO_4^{2-} ions decreases and the value of conductivity gets decreased. Fig. 12 and 13 show change in OD and surface tension at different adsorbent bed doses by using alkali and acid activated charcoal and non-activated charcoal. Results show that elute obtained from alkali activated charcoal has smaller OD and greater surface tension, thus contains smaller SDS as compared to others.

Freundlichand Langmuir adsorption isotherms have studied for various pH values at different initial concentrations. The values of slope (y) and regression co-efficient (R^2) of the isotherms are shown in Table I.

Table I: Table of slope (y) and regression co-Efficient (R^2) of two adsorption isotherms

S.No.	Type of Adsorption Isotherm	Value of	Value of
1	Freundlich	0.2829x - 0.552	0.9623
2	Langmuir	0.2689x - 0.3253	0.9776

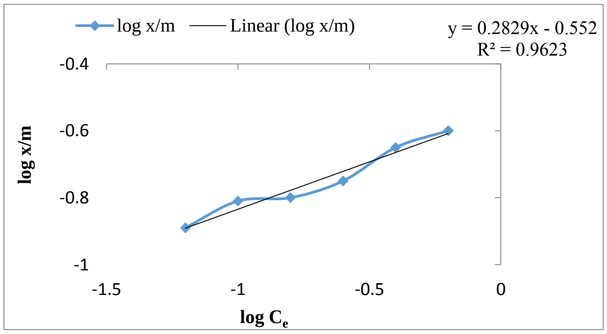


Fig. 14: Plot of freundlich adsorption isotherm for the adsorption of SDS

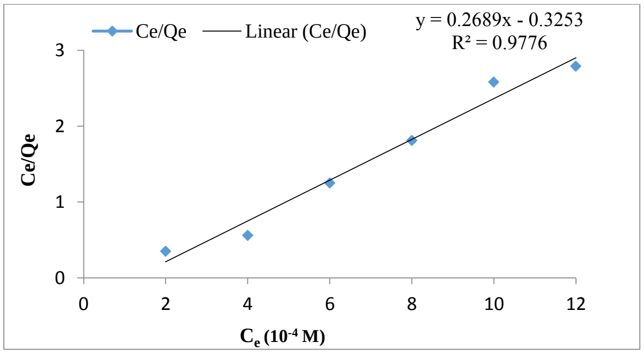


Fig. 15: Plot of langmuir adsorption isotherm for the adsorption of SDS

Fig. 14 and 16 are the plots of Freundlich adsorption isotherm that show the linear plot logC_e Vs log x/m. From this, Regression coefficient (R^2) values obtained are 0.9623 and 0.9781 respectively, which indicate that the adsorption follows Freundlich isotherm model. The values of also indicate acceptability of this isotherm.

Fig. 15 and 17 are the plots of Langmuir adsorption isotherm that show the linear plot C_e Vs C_e/Q_e. From this, Regression coefficient (R^2) values obtained are 0.9776 and 0.9800 respectively, which indicate that the adsorption follows Langmuir isotherm model. The values of designate suitability of this isotherm too.

Freundlichand Langmuir adsorption isotherms have studied for various conductivity values at different initial concentrations. The values of slope (y) and regression co-efficient (R^2) of the isotherms are shown in Table II.

TABLE II: TABLE OF SLOPE (Y) AND REGRESSION CO-EFFICIENT (R^2) OF TWO ADSORPTION ISOTHERMS

S.No.	Type of Adsorption Isotherm	Value of	Value of
1	Freundlich	0.3714x - 0.1252	0.9781
2	Langmuir	0.241x + 0.0313	0.9800

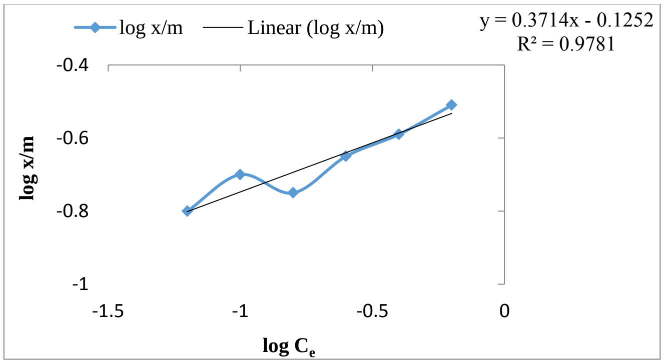


Fig. 16: Plot of freundlich adsorption isotherm for the adsorption of SDS

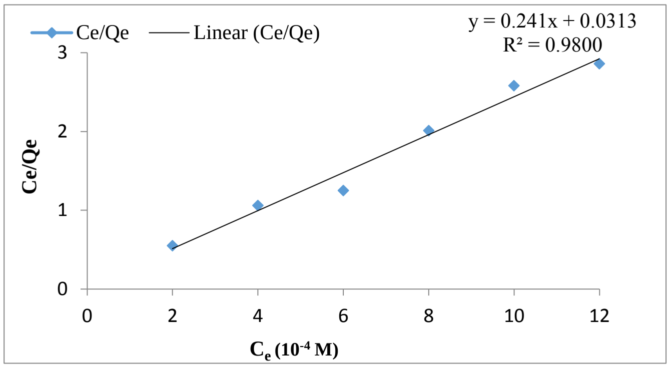


Fig. 17: Plot of langmuir adsorption isotherm for the adsorption of SDS

III. CONCLUSION

Alkali activated adsorbent bed is found to be a better adsorbent bed for removing SDS from waste water. The exclusion of SDS is strongly dependent on adsorbent bed dosages, initial SDS concentration and shaking time. The maximum adsorption of SDS is obtained at C_i $2x10^{-4}$M, adsorbent dosage of 2.0 gram and a contact time of 30 min. The pH, electrical conductivity, spectrophotometric extraction and surface tension parameters favour the results. Twoadsorption isotherms are analyzed here: Freundlichand Langmuir adsorption isotherms. The value of showsadsorption equilibrium data is fitted well to the Langmuir adsorption isotherm.

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