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STUDY ON THE ADSORPTION OF SURFACTANT WITH AND WITHOUT ELECTROLYTES ON ACTIVATED SEASHELL SORBENT

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Abstract

In this study, waste seashell was used as biosorbent for the adsorption of surfactant with and without electrolytes from model aqueous solution at pH 6. Surfactant, Sodium Dodecyl Sulphate (SDS) was used as modifier. The Critical Micelle Concentration (CMC) value of SDS decreased with mixing electrolytes (Na_2SO_4 and Na_3PO_4). Therefore, upon addition of Na_2SO_4 and Na_3PO_4 in SDS, Na_3PO_4 decreased the CMC value of SDS more than Na_2SO_4. Adsorption of SDS on Heat Activated Sea Shell Powder (HASSP-7) sample by batch operations were conducted with different operation parameters such as initial concentration of adsorbate and dosage of adsorbent. The optimum dosage was 0.1 g and initial concentration was 100 ppm. Sorption of SDS on HASSP-7 was conducted with and without electrolytes. The adsorbed amount of SDS was found more with electrolytes than without electrolytes. Moreover, the amount of SDS adsorption with Na_2SO_4 was high in comparison with Na_3PO_4. The outcome of the present research is the surfactant consumption can be reduced by adding small amount of electrolytes to the surfactant solutions. It is expected that they can be used in the treatment of paper industrial wastewater containing surfactant (SDS).

Keywords: seashell, sodium dodecyl sulphate, critical micelle concentration, electrolytes, adsorption

Introduction

Surfactants have two main features, i.e. surface activity and the ability to form micelles in solutions which in turn affects the functionality of surfactants (Caron *et al*., 1995). One of the main characteristics of surfactants is their tendency, in dilute aqueous solutions, to self-assemble and form aggregates by exposing polar head groups to water and segregating hydrophobic tails from water (Antonello *et al*., 2016). The monomers combined in aqueous solution to form big molecules depend on the molecular structures of the surfactant, concentration, temperature and different electrolyte which are added (Lindman and Wennerstrom, 1980). The opposite charged groups of the electrolyte and the surfactant are attracted electrostatically. So, electrolyte works as a pattern for the aggregation of the surfactants, which finally results in the reduction of the repulsive interaction among surfactant head group which facilitate the aggregation behaviour (Neumann and Tiera, 1997). Electrolyte decreases the surface activity of surfactants (Pethica *et al*., 1954) and the CMC and surface tension of aqueous solution decrease in presence of electrolyte.

The critical micelle concentration (CMC) is defined as the concentration above which micelles form. At low surfactant concentration the surfactant molecules arrange on the surface. When more surfactant is added the surface tension of the solution starts to rapidly decrease since more and more surfactant molecules will be on the surface. When the surface becomes saturated, the addition of the surfactant molecules will lead to formation of micelles. This concentration point is called critical micelle concentration. The effect of ionic strength or electrolytes can significantly influence the critical micellar concentration (CMC), surface tension value at CMC and adsorption densities at air-liquid and solid-liquid interfaces which may have great importance in many applications. Electrolyte decreases the value of CMC; because the ions of the electrolytes neutralized the charge on the micelle surface thus decreasing the thickness of ionic compound

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around the surfactant and electrostatic repulsion between them helping in this way to micellization process (Paredes *et al*., 1984).

Sodium dodecyl sulphate has the chemical formula $C_{12}H_{25}NaO_4S$ or CH_3-$(CH_2)_{11}$-O-SO_3-Na^+. SDS is a high production volume chemical. In solution, the sodium cation (Na^+) dissociates from the anionic part of the compound (lauryl or dodecyl sulphate), and this anionic compound is the active chemical. SDS is an anionic surfactant, which is a class of chemicals used for their detergent properties. SDS is a highly effective surfactant and is used in the removal of oily stains and residues. SDS also takes part in an essential function in commerce as leather softening and wool cleaning, metal processing, emulsifier, penetrant in glaze, paint remover and antifoaming agent in solid rocket propellants. It may also use as penetrant, flocculating and de-inking agent in paper industry.

Seashell, crab carapace, palm shell and others have been discovered as a natural biosorbent to remove heavy metal (Kadir *et al*., 2013; Pavan *et al*., 2006). Biosorption process is nonpolluting, easy to operate, offers high efficiency of treatment of wastewaters containing low metal concentrations and possibility of metal recovery (Febrianto *et al*., 2009). The objective of this paper is to study the adsorption behaviour of surfactants in the presence of electrolytes to reduce the surfactant consumption. The presence of electrolyte along with the surfactants in the cleaning process may reduce the consumption of surfactant along with the increase in adsorption and wetting properties. In many cases, after the cleaning process surfactants are disposed in the environment; in this situation, less consumption of surfactant may also reduce environmental problems.

Materials and Methods

Sample Collection

Mussel shell was obtained from fish market in Pathein Township, Ayeyarwady Region.

Preparation of Heat Activated Seashell Powder (HASSP)

The mussel shell was washed with distilled water and dried at room temperature for 2 d. It was also dried in an oven at 105 °C for 2 h. The dried sample was ground with blender and the pulverized shell was sieved through 80 mesh size to achieve Raw Sea Shell Powder (RSSP) (Srividya and Mohanty, 2009). RSSP was calcined in furnace at (400°C to 1000 °C) for 2 h to get heat activated seashell powder (HASSP) and these were designed as HASSP 1-7. Finally, heat activated seashell powder (HASSP 1-7) were obtained.

Determination of Critical Micelle Concentration (CMC) of Sodium Dodecyl Sulphate (SDS) with and without Electrolytes

Different concentrations of sodium dodecyl sulphate solution (1×10^{-3} M to10×10^{-3} M) was prepared with 0.001 M of electrolytes solutions (Na_2SO_4 and Na_3PO_4). These solutions were adjusted at pH 6. Then, 1 mL each sodium dodecyl sulphate solution was placed into the beaker and 2 drops of 0.005 M acridine orange, 2 drops of acetic acid and 5 mLof toluene were added. Then, it was shaken with a separating funnel for 1 min and allowed to stand for 5 min. The aqueous layer was discarded. The toluene layer was collected and measured by UV-Visible spectrophotometer at λ_{max} 498 nm and 25 °C. The absorbance and concentration of sodium dodecyl sulphate was plotted and the CMC value was determined from the breaking point of the CMC.

Sorption Studies of More Activated Seashell Sorbent

For the adsorption experiment, sodium dodecyl sulphate solution (100 ppm) was mixed with 0.001 M of electrolyte solution (Na_2SO_4 and Na_3PO_4). All the measurements were carried out at pH 6. Then, 0.1 g of heat activated seashell powder at 1000 °C (HASSP-7) was added into the

100 mL of above the mixture solution. It was shaken with electric shaker for 1 h and filtered. Then, 10 mL of filtrate solution was taken and added 2 drops of 0.005 M acridine orange, 2 drops of glacial acetic acid and 5 mL of toluene. The contents were shaken with separating funnel for 1 min and allowed to stand for 5 min. The aqueous layer was discarded. The toluene layer was collected and measured by UV-Vis spectrophotometer at λ_{max} 498 nm and adsorption data were computed. Similarly,the above procedure was carried out using 25,50,75,125 and 150 ppm sodium dodecyl sulphate solutions to study the effects of initial concentration solutions. To investigate the effect of dosage of HASSP on the removal of SDS, the different amounts of HASSP-7 (0.1,0.2,0.3,0.4 and 0.5 g) were used.

Results and Discussion

Critical Micelle Concentration (CMC) of SDS with and without Electrolytes

The critical micelle concentration (CMC) values of sodium dodecyl sulphate (SDS) with and without electrolytes (Na_2SO_4 and Na_3PO_4) are shown in Table 1 and Figure 1. Here, the CMC value of SDS decreased with mixing electrolytes. It may be due to partial neutralization of anionic head group negative charge by electrolyte cations (Berr and Jones, 1988). Therefore, upon addition of Na_2SO_4 and Na_3PO_4 in SDS, Na_3PO_4 is more effective in reducing the CMC value of SDS. In this research, Na_3PO_4 decreased the CMC value of SDS more than Na_2SO_4.

Table 1 Critical Micelle Concentration (CMC) of SDS with and without Electrolytes

Concentration (10^{-3}M)	Absorbance*		
	SDS without electrolytes	SDS with Na_2SO_4	SDS with Na_3PO_4
1	0.286	0.277	0.263
2	0.275	0.264	0.248
3	0.286	0.273	0.261
4	0.268	0.259	0.231
5	0.215	0.204	0.173
6	0.262	0.235	0.222
7	0.296	0.288	0.258
8	0.283	0.261	0.247
9	0.317	0.295	0.275
10	0.296	0.266	0.242

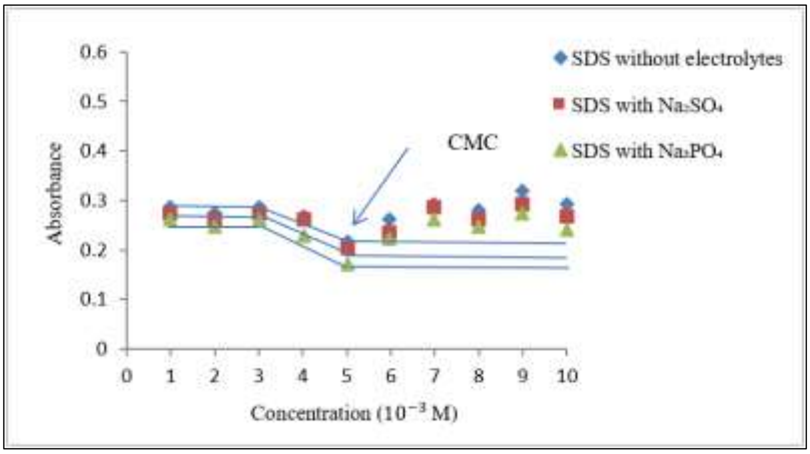

Figure 1 Critical micelle concentration (CMC) of SDS with and without electrolytes Electrolytes = Na_2SO_4 and Na_3PO_4, pH = 6, SDS = sodium dodecyl sulphate

Effect of Initial Concentration of SDS on the Adsorption of SDS by HASSP-7

In this research, the effect of initial concentration of SDS was studied by varying SDS concentrations (25 ppm to 150 ppm) for the removal of SDS. It was found that the highest adsorbed amount of SDS by HASSP-7 was 51.25 mg/g in 100 ppm concentration of SDS. The results are shown in Table 2 and Figure 2.

Table 2 Effect of Initial Concentration of SDS on the Adsorption of SDS by HASSP-7

No	Initial concentration of SDS (ppm)	q_e (mg/g)
1	25	5.11
2	50	12.29
3	75	37.92
4	100	51.25
5	125	38.47
6	150	27.29

HASSP-7 = Heat Activated Seashell Powder at 1000 ºC, Shaking time = 60 min
SDS = Sodium Dodecyl Sulphate, Dosage = 0.1 g, pH = 6, λ_{max} = 498 nm

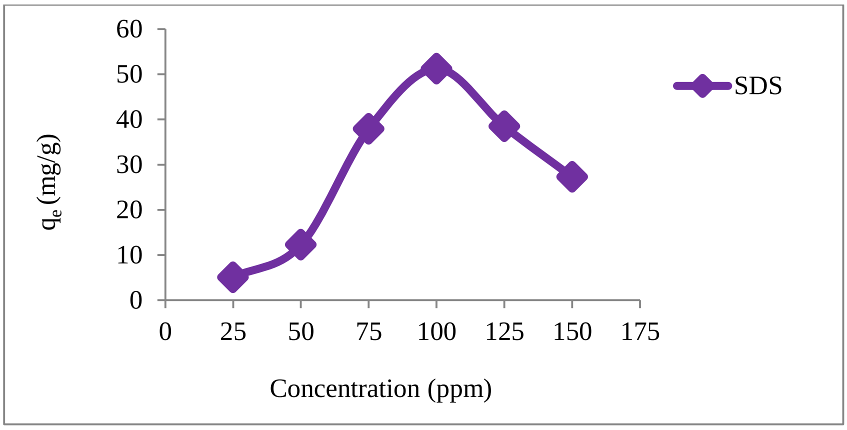

Figure 2 Effect of initial concentration of SDS on the adsorption of SDS by HASSP-7

Effect of Dosage of HASSP-7 on the Adsorption of SDS

In this research work, the different dosage amounts of HASSP-7 (0.1 g to 0.5 g) was carried out for the removal of SDS. It was observed that the optimum dosage was 0.1 g. In the case, the adsorbed amount was decreased with increasing adsorbent mass. Therefore, it was indicated that the increase in SDS adsorption efficiency is not directly proportional to adsorbent mass. The results are shown in Table 3 and Figure 3.

Table 3 Effect of Dosage of HASSP-7 on the Adsorption of SDS

No.	Dosage of Adsorbent (g)	q_e (mg/g)
1	0.1	60.55
2	0.2	25.82
3	0.3	17.13
4	0.4	12.61
5	0.5	9.33

HASSP-7 = Heat Activated Seashell Powder at 1000 ºC, Shaking time = 60 min
Initial concentration = 100 ppm, Stirring rate = 200 rpm, pH = 6, λ_{max} 498 nm

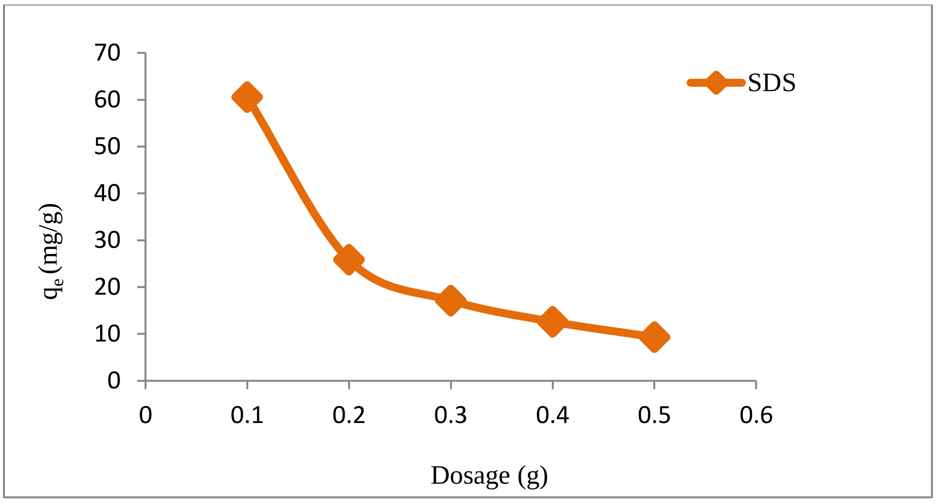

Figure 3 Effect of dosage of HASSP-7 on the adsorption of SDS

Adsorption of SDS with and without Electrolytes on HASSP-7

The adsorption efficiencies of HASSP-7 were determined on the adsorption of SDS with and without electrolytes (Na_2SO_4 and Na_3PO_4) at the optimum condition. It was indicated that the adsorbed amount of SDS without electrolytes was 51.29 mg/g. The amount of SDS adsorption with Na_2SO_4 and Na_3PO_4 were 75.62 mg/g and 65.63 mg/g, respectively. Here, the adsorption of SDS with electrolytes was found to be higher than that without electrolytes. Furthermore, the adsorption capacities of SDS with Na_2SO_4 was high in comparison with Na_3PO_4. The results are shown in Table 4 and Figure 4.

Table 4 Adsorption of SDS with and without Electrolytes on HASSP-7

No	HASSP-7	q_e (mg/g)
1	SDS without electrolytes	51.29
2	SDS with Na_2SO_4	75.62
3	SDS with Na_3PO_4	65.63

Electrolytes = Na_2SO_4 and Na_3PO_4 (0.001M), SDS = Sodium dodecyl sulphate
HASSP-7 = Heat activated seashell powder at 1000˚C, λ_{max} = 498 nm
SDS concentration = 100 ppm, Dosage = 0.1 g, Shaking time = 60 min

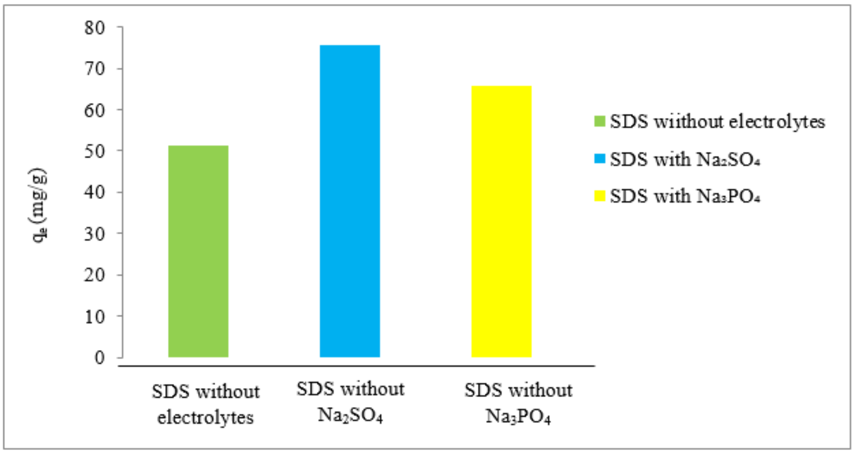

Figure 4 Adsorption of SDS with and without electrolytes on HASSP-7

Conclusion

In this research work, the critical micelle concentration (CMC) values of SDS with electrolytes (Na_2SO_4 and Na_3PO_4) were more effectively reduced than without electrolytes. Moreover, the CMC value of SDS in the presence of Na_3PO_4 decreased more than Na_2SO_4. For the adsorption of HASSP-7 the optimum conditions were initial concentration of SDS as 100 ppm and dosage as 0.1 g. Sorption of SDS on HASSP-7 sample was conducted with and without electrolytes. The amount of SDS adsorption without electrolytes was 51.29 mg/g and those with Na_2SO_4 and Na_3PO_4 were 75.62 mg/g and 65.63 mg/g, respectively. The adsorption of SDS with electrolytes was more than without electrolytes. Furthermore, the adsorbed amount of SDS on HASSP-7 was found to be more than those in the presence of Na_2SO_4 than Na_3PO_4. The contribution of this study is that the surfactant consumption can be reduced by adding small amount of electrolytes to the surfactant solutions and they can be used in the treatment of paper industrial wastewater containing surfactant (SDS).

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