

STUDY ON SORPTION PROPERTIES OF ACTIVATED BIOSORBENTS (FISHSCALE AND SEASHELL) FOR THE REMOVAL OF ANIONIC SURFACTANT

Myint Myint Than¹, Nwe Nwe Aung², Aye Thant Zin³

Abstract

In this study, waste fishscale and seashell were used as biosorbents for the removal of surfactants from industrial wastewater. These biosorbents were collected from fish market in Patheingyi Township, Ayeyarwady Region. The selected samples were washed with distilled water for three times and were soaked in 3 % nitric acid for 24 h and then were washed again with distilled water until pH 7 and dried in an oven at 105°C and were made to powder form. The physicochemical properties such as moisture content, bulk density and pH of raw fishscale powder (RFSP) and raw seashell powder (RSSP) were determined by conventional methods and characterized by modern techniques such as EDXRF, SEM, TG-DTA and FT IR analyses. RFSP and RSSP were calcined at various temperatures (400°C to 1000°C) to obtain heat activated fishscale powder 1-7 (HAFSP 1-7) and heat activated seashell powder 1-7 (HASSP 1-7). The critical micelle concentration (CMC) of sodium dodecyl sulphate (SDS) were obtained as 7×10^{-3} M, 7×10^{-3} M, 7×10^{-3} M, 4×10^{-3} M, 6×10^{-3} M and 5×10^{-3} M at pH 1, 2, 3, 4, 5 and 6 respectively. From these results, 7×10^{-3} M at pH 3 and 5×10^{-3} M at pH 6 were selected as optima CMC of SDS. The adsorption properties of different biosorbents (HAFSP-1, 2, 3, 4, 5, 6 and 7) and (HASSP-1, 2, 3, 4, 5, 6 and 7) were compared for the removal of SDS at pH 3 and 6. According to these analyses, HAFSP-5 and HASSP-7 were found to be more effective than other samples. Adsorption capacities of HAFSP-5 and HASSP-7 were determined at different contact time and pH by using UV-Vis spectrophotometer at λ_{\max} 498 nm and 25°C. The optimum contact time was 60 min and pH were 3 and 6 respectively for the removal of SDS solution from the paper industrial wastewater by HAFSP-5 and HASSP-7. The outcome of the present research is the preparation of waste biosorbents for the removal of anionic surfactants from the paper industrial wastewater.

Keywords: fishscale, seashell, sodium dodecyl sulphate, critical micelle concentration, biosorbents

Introduction

Surfactants are surface active agents with a diverse group of chemicals consisting of a polar, water-soluble head group and a nonpolar hydrocarbon tail group. They are widely used in household and industrial products (Eriksson *et al.*, 2008; Reemtsma *et al.*, 2006). After use, residual surfactants are discharged into sewage systems or directly into surface water and most of them end up dispersed in different environmental compartments such as soil, water or sediment. They are harmful to human beings, fishes and vegetation and are responsible to cause foams in rivers and effluent treatment plants and to reduce the quality of water. They cause short term as well as long term changes in ecosystem (Sigoillot and Nguyex, 1992; Margesin and Schinner, 1998; Eichhorn *et al.*, 2001, 2002). They are classified into four main groups: anionic, nonionic, cationic and zwitterionic (amphoteric).

Surfactants can assume several supramolecular arrangements in solution, including circular aggregates called micelles. Micelles are formed when the surfactant concentration reaches a certain value, termed the critical micelle concentration (CMC). They are arranged with hydrophobic tails oriented inward and hydrophilic heads oriented toward the aqueous solution. Fishscale (FS) and seashell (SS) are waste product and abundant. The cell wall surface of biosorbents contained several of functional groups for surfactants attached onto adsorbents and the porous layer may provide a good possibility of surfactants to be adsorbed on its surface

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(Kumar *et al.*, 2008; Nadeem *et al.*, 2008; Vieira *et al.*, 2011). Almost all the methods for spectrophotometric determination of anionic surfactants are based on the formation of ion associates and their subsequent extraction into organic solvents. In this paper, the removal of anionic surfactant from industrial wastewater was conducted by using activated biosorbents (Fishscale and Seashell).

Materials and Methods

Preparation of Biosorbents

Waste fishscale and seashell were collected from fish market in Patheingyi Township, Ayeyarwady Region. The fishscales were washed first with distilled water and were soaked in 3% nitric acid for 24 h and then were washed again with distilled water until pH 7. The seashell were washed with distilled water to remove any adhering impurities. They were dried in an oven at 105 °C for 2 h. The dried raw fishscale powder (RFSP) and raw seashell powder (RSSP) were obtained by grinding with mortar and pestle followed by sieving (Srividya and Mohanty, 2009). RFSP and RSSP were calcined at various temperatures (400 °C to 1000 °C) to obtain heat activated fishscale powder 1-7 (HAFSP 1-7) and heat activated seashell powder 1-7 (HASSP 1-7).

Preparation of Stock Solution

Acridine orange (ACO) was used for the preparation of 5×10^{-3} M solution to be used as a stock. Sodium dodecyl sulphate (SDS) was purchased from BDH, Yangon Region. Toluene was used as an extractant. Glacial acetic acid was used to maintain the pH during extraction.

Determination of Physicochemical Properties of Raw Fishscale Powder (RFSP) and Raw Seashell Powder (RSSP)

Determination of bulk density

A clean dry 10 mL graduated measuring cylinder was weighed. It was filled with the dry powder sample to reach the mark and reweighed. The graduated cylinder was placed in a tapping box and the cylinder was tapped gently with several times until no more reduction in volume. The minimum volume was recorded and the bulk density was calculated.

Determination of Critical Micelle Concentration (CMC) of Sodium Dodecyl Sulphate (SDS)

The various concentration of SDS solution were prepared from 1×10^{-3} M to 10×10^{-3} M. This solution were maintained at pH 1, 2, 3, 4, 5 and 6. 0.5 mL of each concentration was placed into a beaker and 5 mL of toluene was added followed by the addition of 2 drops each of acridine orange and glacial acetic acid. The contents were shaken with separating funnel for 1 min and allowed to settle for 5 min. The toluene layer was discarded and it was measured by using UV-Vis spectrophotometer at λ_{\max} 498 nm and 25°C.

Experimental Procedure

0.1 g of heat activated fishscale powder (HAFSP 1-7) was added into 100 mL of surfactant solution. It was shaken with electric shaker and filtered. This solution (10 mL) was placed into a beaker and 5 mL of toluene was added followed by the addition of 2 drops each of acridine orange and glacial acetic acid. The contents were shaken with separating funnel for 1 min and allowed to settle for 5 min. The toluene layer was discarded and it was measured by

using UV-Vis spectrophotometer at λ_{max} 498 nm and 25°C. Similarly, heat activated seashell powder (HASSP 1-7) was operated by using the above method.

Results and Discussion

Physicochemical Properties of Raw Fishscale Powder (RFSP) and Raw Seashell Powder (RSSP) Samples

The physicochemical properties such as moisture content, bulk density and pH of raw fishscale powder (RFSP) and raw seashell powder (RSSP) samples presented in Table 1. It was found that RFSP was higher than RSSP in moisture content. However, RSSP was higher than RFSP in bulk density and pH.

Table 1 Physicochemical Properties of Raw Fishscale Powder (RFSP) and Raw Seashell Powder (RSSP) Samples

Sample	Moisture (%)	Bulk Density (gcm ⁻³)	pH
RFSP	9.77	0.79	6.8
RSSP	0.64	1.76	9.3

EDXRF Analysis

In this research, according to EDXRF spectra, RFSP contained calcium oxide as the major constituent and phosphorus(V) oxide as the second major constituent and other trace constituents. RSSP contained carbon dioxide as the major constituent, calcium oxide as the second major constituent and other trace constituents (Figures 1, 2 and Table 2).

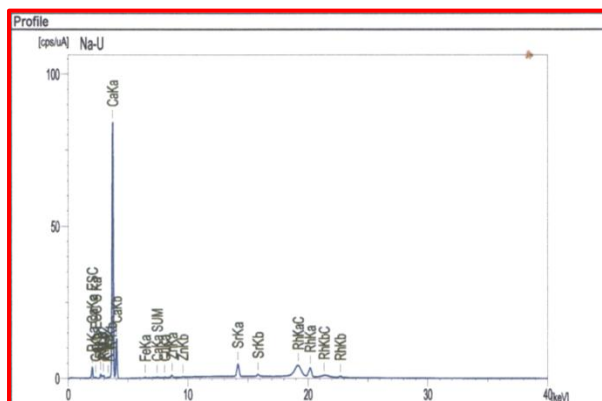


Figure 1 EDXRF spectrum of raw fishscale powder (RFSP)

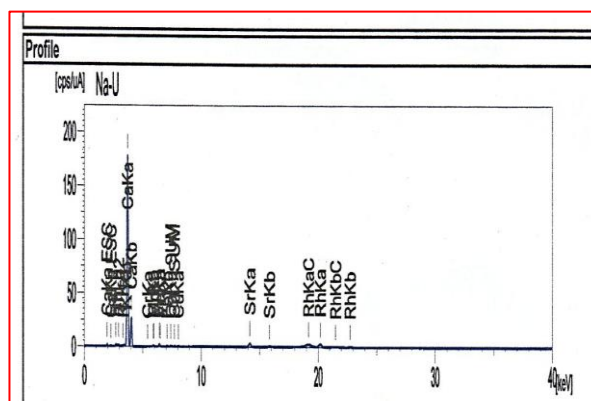


Figure 2 EDXRF spectrum of raw seashell powder (RSSP)

Table 2 Results from EDXRF Spectrum of Raw Fishscale Powder (RFSP) and Raw Seashell Powder (RSSP)

Constituents	Relative Abundance of Some metallic Oxide (%)	
	RFSP	RSSP
CaO	59.018	48.584
P ₂ O ₅	39.254	-
SO ₃	1.023	-
K ₂ O	0.391	0.287
SrO	0.180	0.075
ZnO	0.062	-
Fe ₂ O ₃	0.057	0.201
CuO	0.014	0.010
MnO	-	0.120
Cr ₂ O ₃	-	0.014
CO ₂	-	50.710

SEM Analysis

SEM micrographs of RFSP and RSSP are indicated in Figures 3 and 4. In these SEM micrograph, RFSP was observed as non-porous structure and RSSP as rough and disordered surface with low porosity grains.

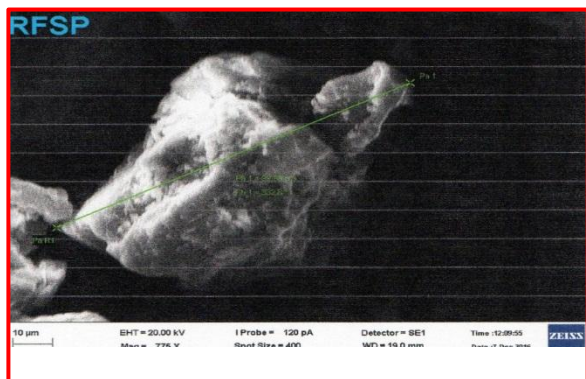


Figure 3 Scanning electron micrograph of raw fishscale powder (RFSP)

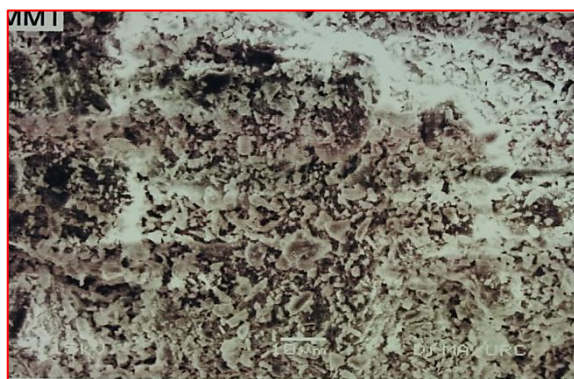


Figure 4 Scanning electron micrograph of raw seashell powder (RSSP)

FT IR Analysis

FT IR spectra of RFSP and RSSP are presented in Figures 5 and 6. The broad bands at 3460 and 3454 cm⁻¹ are assigned to stretching vibration of O-H bonds. The bands observed between 2950 and 2940 cm⁻¹ are assigned to C-H stretching groups. The results are shown in Table 3.

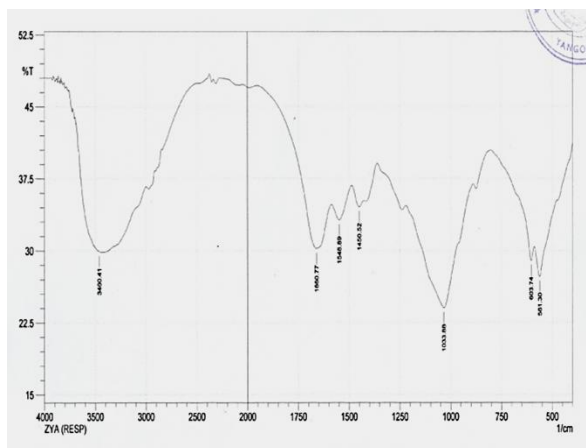


Figure 5 FT IR spectrum of raw fishscale powder (RFSP)

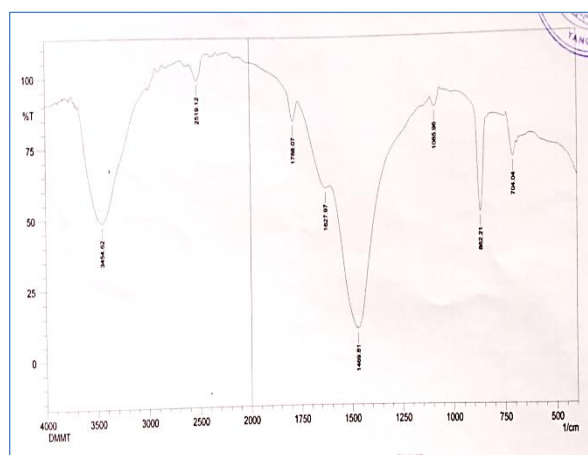


Figure 6 FT IR spectrum of raw seashell powder (RSSP)

Table 3 Absorption Bands and Assignment of FT IR Spectral Data of RFSP and RSSP

Observed Frequency (cm ⁻¹)		Reference *	Possible Assignment
RFSP	RSSP		
3460	3454	3700-3200	Stretching vibration of O-H bonds
2950	2940	2980-2850	C-H stretching
-	1788	1810-1790 (s)	C=O stretching
1660	1627	1670-1640	Stretching vibration of C=O bonds
1548	-	1600-1400	C=C stretching
1450	1469	1625-1430	C=C stretching of aromatic ring
1033	1085	1100-1000	P-O-C stretching vibration
-	862	890-850 (s)	C-C stretching
-	704	705-570	C-C stretching
603	-	615-535	C=O out of plane bending

*Silverstein *et al.*, (2003)

TG-DTA Analysis

In this experiment, the weight loss percent of RFSP was found to be 7.87 % due to the dehydration of surface water and moisture and there was endothermic peak at 80.53 °C. The exothermic peak was observed at about 370.13 °C and weight loss was 18.55 % due to the decomposition of volatile materials. The third weight loss was 14.44 % due to the decomposition and combustion of residual organic components at the temperature range of 380 °C to 600 °C (Figure 7 and Table 4). In RSSP, no weight loss was observed due to the absence of moisture and absorbed water at the temperature range of 38-280 °C. The exothermic peak was observed at about 361-450 °C due to the removal of organic volatile materials (Figure 8 and Table 5).

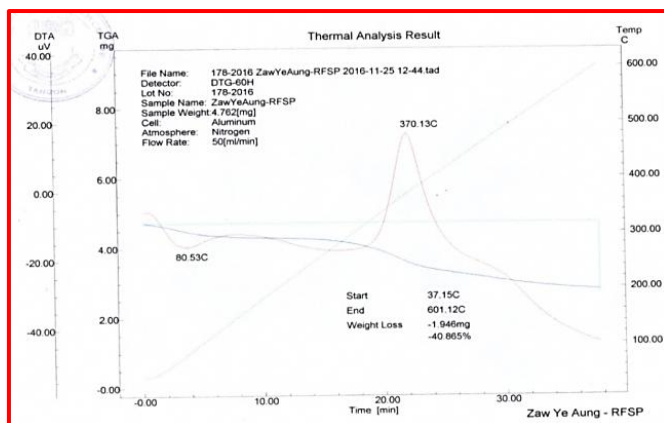


Figure 7 TG-DTA thermogram of raw fishscale powder (RFSP)

Table. 4 TG-DTA Thermal Analysis Data of Raw Fishscale Powder (RFSP)

Temp: range (°C)	Weight loss (%)	Peak's Temperature (°C)	Nature of Peak	TG Remark
37-120	7.87	80.53	endothermic	- This weight loss is due to the removal of surface water and moisture
120-380	18.55	370.13	exothermic	- The second weight loss is due to the decomposition of volatile materials
380-600	14.44	-	-	- The third weight loss is due to the decomposition and combustion of residual organic components in the fish scales sample

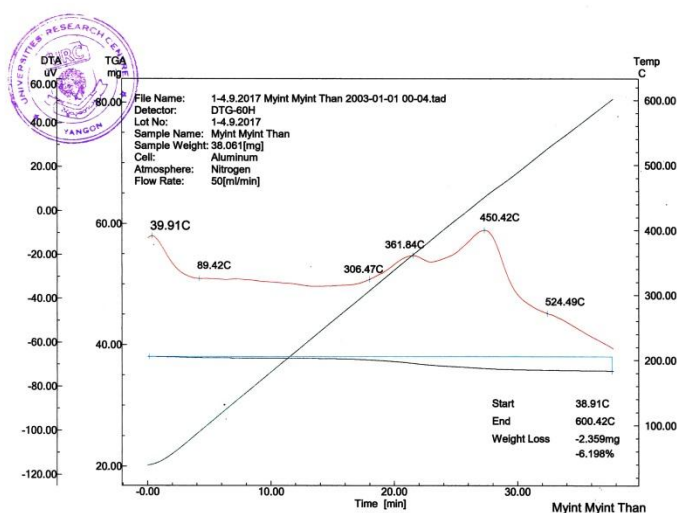


Figure 8 TG – DTA thermogram of raw seashell powder (RSSP)

Table 5 TG-DTA Thermal Analysis Data of Raw Seashell Powder (RSSP)

Temp: range (°C)	Weight loss (%)	Peak's Temperature (°C)	Nature of Peak	TG Remark
38-280	-	-	-	- No weight loss due to the absence of moisture and absorbed water.
280-600	6.19	361-450	exothermic	-This weight loss was due to the removal of organic volatile materials.

Determination of Critical Micelle Concentration (CMC) of Sodium Dodecyl Sulphate (SDS)

The literature reported value for the CMC of SDS in water is 8.1×10^{-3} M (Haigh *et al.*, 1996). In this experiment, CMC of SDS were obtained as 7×10^{-3} M, 7×10^{-3} M, 7×10^{-3} M, 4×10^{-3} M, 6×10^{-3} M and 5×10^{-3} M at pH 1, 2, 3, 4, 5 and 6 respectively. The optima CMC of SDS were 7×10^{-3} M at pH 3 and 5×10^{-3} M at pH 6. The results are shown in Tables (6-7) and Figures (9-14).

Table 6 CMC of SDS at pH 1, 2, 3, 4, 5 and 6 at 25°C

Concentration ⁻³ (10 M)	Absorbance					
	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6
1	0.323	0.819	0.683	0.223	0.256	0.286
2	0.491	0.337	0.398	0.269	0.228	0.275
3	0.512	0.373	0.532	0.259	0.220	0.286
4	0.523	0.396	0.499	0.220	0.237	0.268
5	0.372	0.327	0.521	0.255	0.246	0.224
6	0.376	0.391	0.374	0.271	0.234	0.262
7	0.273	0.253	0.219	0.243	0.252	0.296
8	0.573	0.329	0.33	0.240	0.274	0.283
9	0.25	0.269	0.28	0.201	0.269	0.317
10	0.635	0.299	0.373	0.239	0.248	0.296

Table 7 Critical Micelle Concentration (CMC) of SDS at pH 1,2,3,4,5 and 6 at 25°C

pH	Critical Micelle Concentration (CMC)
	⁻³ (10 M)
1	7
2	7
3	7
4	4
5	6
6	5

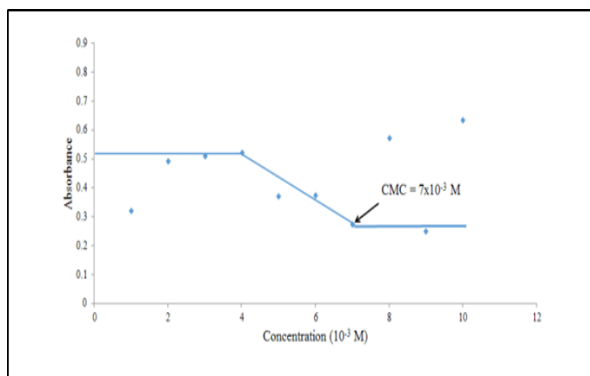


Figure 9 CMC of SDS at pH 1 and 25°C

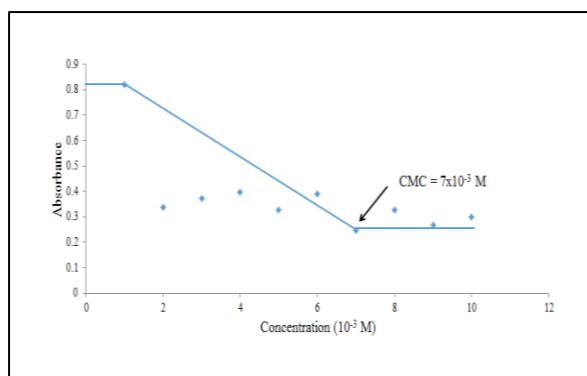


Figure 10 CMC of SDS at pH 2 and 25°C

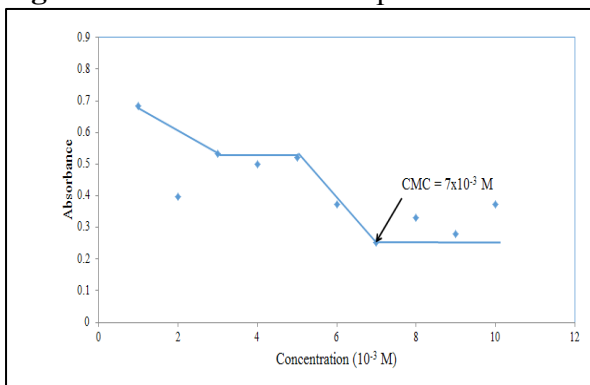


Figure 11 CMC of SDS at pH 3 and 25°C

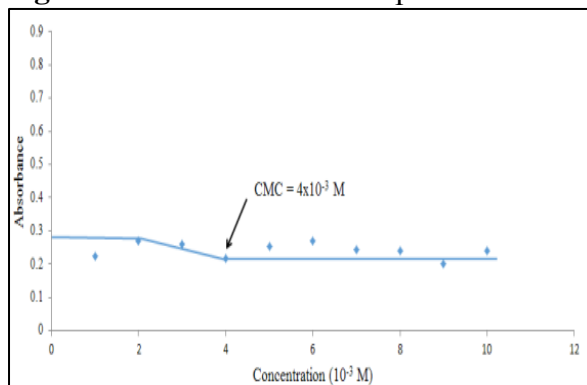


Figure 12 CMC of SDS at pH 4 and 25°C

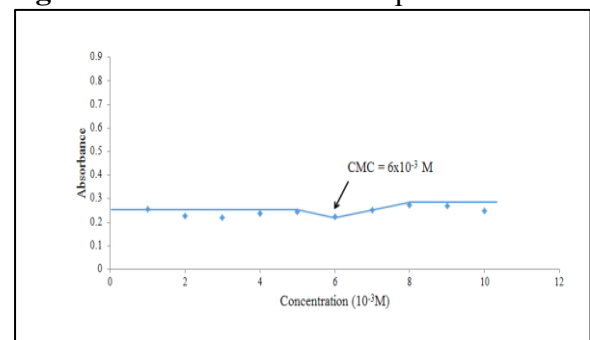


Figure 13 CMC of SDS at pH 5 and 25°C

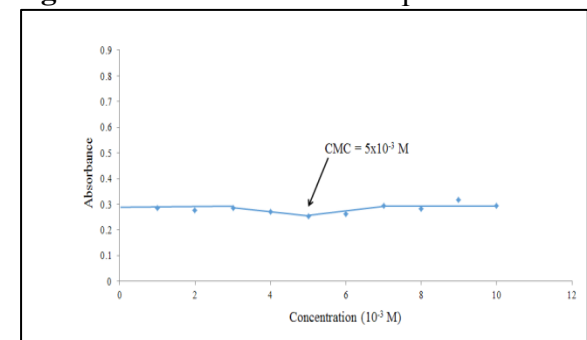


Figure 14 CMC of SDS at pH 6 and 25°C

Comparison of the Adsorption Properties of Heat Activated Fishscale Powder 1-7 (HAFSP 1-7) and Heat Activated Seashell Powder 1-7 (HASSP 1-7)

Adsorption properties of biosorbents (HAFSP and HASSP) activated at (400 °C to 1000 °C) were compared for the removal of SDS at pH 3 and 6. It was found that, HAFSP-5 and HASSP-7 were more effective than other samples. The results are shown in Table 8 and Figure 15 for pH 3 and Table 9 and Figure 16 for pH 6.

Table 8 Comparison of the Adsorption Capacities of the Different Samples of Raw and (HAFSP 1-7) at pH 3 and 25°C

Time (min)	q _t (mg/g)							
	Raw	HAFSP 1	HAFSP 2	HAFSP 3	HAFSP 4	HAFSP 5	HAFSP 6	HAFSP 7
60	25.44	27.33	32.11	37.22	48.61	51.55	47.96	47.55
120	26.34	27.67	30.34	36.77	47.15	50.34	45.46	46.87
180	25.22	23.54	31.54	35.27	48.54	50.55	46.89	47.78

Initial concentration of SDS = 100 ppm
 Dosage of HAFSP = 0.1 g
 pH = 3
 Stirring rate = 200 rpm

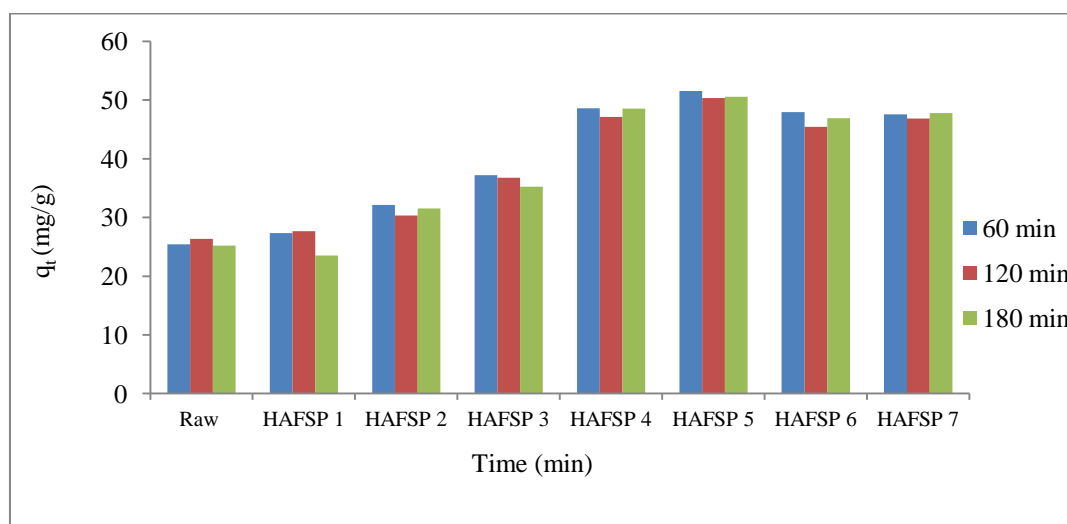
$$q_t = \frac{C_0 - C_e}{\text{mass of adsorbent}} \times \text{volume of solution}$$


Figure 15 Comparison of the adsorption capacities of the different samples of raw and (HAFSP 1-7) at pH 3 and 25°C

Table 9 Comparison of the Adsorption Capacities of the Different Samples of Raw and (HASSP 1-7) at pH 6 and 25°C

Time (min)	q _t (mg/g)							
	Raw	HASSP 1	HASSP 2	HASSP 3	HASSP 4	HASSP 5	HASSP 6	HASSP 7
60	24.11	27.78	28.92	29.87	32.53	34.61	36.42	49.80
120	24.82	30.45	27.85	28.41	28.95	30.52	32.91	49.43
180	25.43	29.10	27.63	29.21	32.43	34.51	36.35	48.45

Initial concentration of SDS = 100 ppm
 Dosage of HASSP = 0.1 g
 pH = 6
 Stirring rate = 200 rpm

$$q_t = \frac{C_0 - C_e}{\text{mass of adsorbent}} \times \text{volume of solution}$$

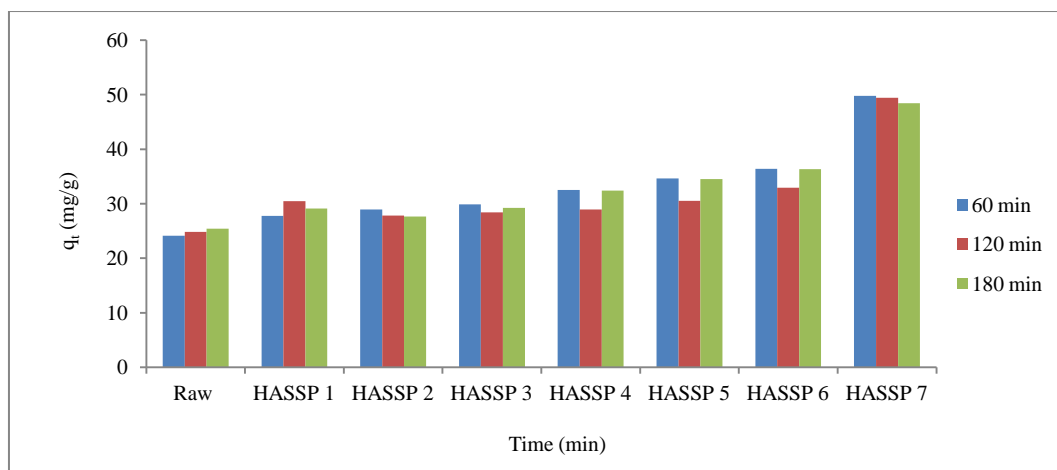


Figure 16 Comparison of the adsorption capacities of the different samples of raw and (HASSP 1-7) at pH 6 and 25°C

Effect of Different Contact Time and pH on the Removal of SDS by HAFSP-5 and HASSP-7

Adsorption capacities of HAFSP-5 and HASSP-7 were determined with different contact time and pH by using UV-Vis spectrophotometer at λ_{\max} 498 nm and 25°C. It was observed that the optimum contact time for removal of SDS by HAFSP-5 and HASSP-7 was 60 min (Table 10 and Figure 17) and the pH optima were 3 and 6 by HAFSP-5 and HASSP-7, respectively (Table 11 and Figure 18).

Table 10 Effect of Contact Time on the Removal of SDS by HAFSP-5 (pH 3) and HASSP-7 (pH 6)

Time (min)	q_t (mg/g)	
	HAFSP-5 (pH 3)	HASSP-7 (pH 6)
30	34.42	30.11
60	51.61	49.89
90	50.64	48.72
120	50.46	49.50
150	50.12	48.95
180	49.63	48.57

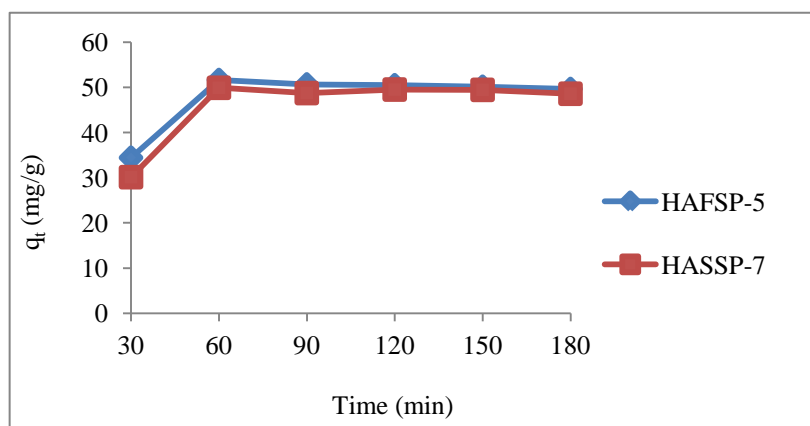


Figure 17 Effect of contact time on the removal of SDS by raw and HAFSP-5 (pH 3) and HASSP-7 (pH 6)

Table 11 Effect of pH for the Removal of SDS by HAFSP-5 and HASSP-7 at 60 min and 25°C

pH	q_t (mg/g)	
	HTFSP-5	HTSSP-7
1	25.42	48.54
2	44.38	7.29
3	68.54	51.46
4	31.04	42.71
5	59.58	39.79
6	51.67	57.92
7	53.78	55.34
8	57.5	56.87
9	59.38	57.79
10	54.17	46.88

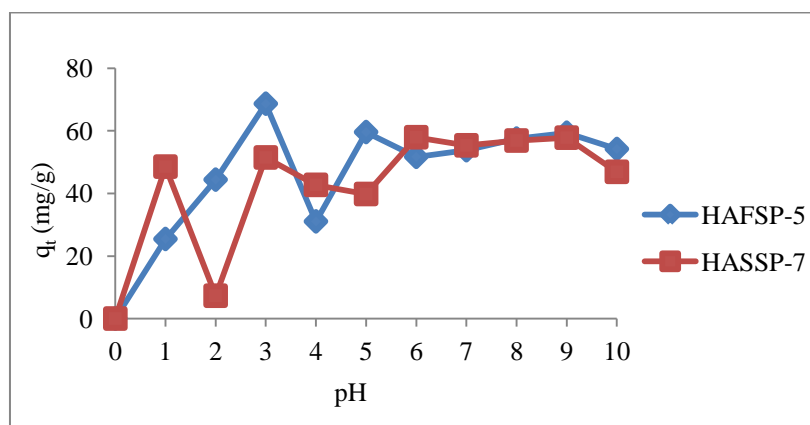


Figure 18 Effect of pH for the removal of SDS by HAFSP-5 and HASSP-7 at 60 min and 25°C

Conclusion

In this research work, the moisture percent of RFSP and RSSP was found to be 9.77% and 0.64%. From EDXRF spectrum, the preparing samples show CaO and CO₂ for major constituent and P₂O₅, SO₃, K₂O, SrO, ZnO, Fe₂O₃, CuO, MnO and Cr₂O₃ for second major constituent. From SEM results, RFSP was non-porous structure and RSSP was rough and disordered surface. In this experiment, the critical micelle concentration (CMC) of sodium dodecyl sulphate (SDS) were 7×10^{-3} M at pH 3 and 5×10^{-3} M at pH 6. HAFSP-5 and HASSP-7 were more effective among other samples. Adsorption capacities of selected samples HAFSP-5 and HASSP-7 at optima contact time and pH were 60 min and pH 3 and 6 for the removal of SDS solution at λ_{max} 498 nm and 25°C. The contribution of this study is that fishscale and seashell samples can be utilized as biosorbents in wastewater treatment.

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