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Research note

Removal of Surfactants from wastewater by Rice Husk

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Abstract

Surfactants are one of the major components (10- 18%) of detergents and household cleaning products and are used in high volumes in developed countries. In the present research work, the ability of rice husk as a low cost adsorbent for anionic and nonionic surfactants in wastewater has been studied.

The maximum removal efficiency for anionic surfactants was 97%, in an aqueous solution that contains 10mg/lit sodium linear alkyl benzene sulphonate in pH 2 and for nonionic surfactants was up to 75% in an aqueous solution that contains 20mg/lit nonyl phenol ethoxylate in pH 6-7.

The mechanism of surfactant removal by rice husk was attributed to the physicochemical characteristics of rice husk. In addition, the size of micelles and critical micelle concentration are two important factors in the removal yield.

Keywords: *Rice husk, Adsorption, Surfactants, Wastewater*

Introduction

Surfactants are synthetic organic chemicals used in high volumes in detergents, personal care and household cleaning products. These compounds usually comprise 10-18% of granular and liquid detergents [1]. Surfactants are also used by the oil, textile, food and mining industries. Although there are many surfactant types, linear alkylbenzene sulfonates (LABS), alkyl sulfates (AS), alkyl ether sulfates (AES), alkyl ethoxylates (AE), alkyl phenol ethoxylates (APE) and quarternary ammonium halide compounds are common in commercial detergent applications [1].

The consumption of two anionic surfactants; linear alkyl benzene sulfonates and alkyl ether sulfates in Iran is estimated at 150,000 ton/year.

The LABS concentrations in sewage have been reviewed [2]. Raw domestic wastewaters have LABS concentrations in the range of 0.54-21 mg/L. Primary treatment results in low removal rates (0-26%) with typical LABS concentrations in effluent of 1.7-2.5 mg/L [3]. Activated sludge treatment removes more than 95%of LABS, providing effluent LABS concentrations of 0.01-0.40 mg/L [3]. However, trickling filter treatment results in higher effluent LABS concentrations of 0.3-1.2 mg/L [4]. There have been a number of monitoring studies of LABS in surface waters [5]. Most of these were conducted from the ecotoxicological pers-

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pective because the toxicity of LABS to aquatic organisms is of concern when concentrations exceed 0.1 mg/L [5].

Alkyl phenol ethoxylates (APE) are nonionic surfactants made up of a branched chain ethylene oxide to produce an ethoxylated chain. Alkyl phenol ethoxylates (APE) are among the most widely used groups of surfactants. World wide, about 500,000 tons are produced annually for use in detergents, paints, pesticides, textile and petroleum recovery chemicals, metal working fluids, and personal care products [6]. Recent evidence that some APE breakdown products are weakly estrogenic has intensified concern over their environmental and human health effects.

One of the methods employed for removing contaminants from wastewater is adsorption. Adsorption capacity for specific single organic solutes of a homologous series is thought to be a direct function of:

1- The adsorbate properties, such as functionality, branching or geometry, polarity, hydrophobicity, dipole moment, molecular weight and size, and aqueous solubility
2- The solution conditions, such as pH, temperature, pressure, adsorbate concentration, ionic strength, and presence of background and competitive solutes
3- The nature of the adsorbent, such as surface area, pore size and distribution, surface distribution, and surface characteristics [7].

The process of adsorption implies the presence of an adsorbent, a solid that binds molecules by physical attractive forces, ion exchange or chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable and economical.

There are a few reports about the use of agricultural byproducts for pollutant removal [8, 9]. Rice bran effectively removed pesticides from an aqueous solution [10]; also, removal efficiency of mono chloramine by rice bran was investigated over range of pH 3-12 [11]. The removal of mono chloramines by rice bran was attributed to its decomposition by direct reaction with rice bran. Some of agricultural byproducts were used for adsorption of heavy metals from wastewater [12]. Adsorption of metal ions by agricultural byproducts may involve metal interaction or coordination to functional groups present in natural proteins, lipids and carbohydrates positioned on cell walls [13].

In this study we have used rice husk as an adsorbent for removing surfactants from wastewater, and we have investigated in above factors.

Husk is a layer of cellulose protecting rice grain. Generally rice producers processing 1 ton of rice obtain 240kgs of husks.

Experimenal

The surfactants used in this project, containing linear sodium alkyl benzene sulfunate **LABS** 50%, sodium lauryl ether sulfate **AES** 70% (anionic surfactants) and nonyl phenol ethoxylate **NPE** (nonionic surfactant) were provided by Paksan Company (a detergent producer in Iran). The solvents were from Pars Iran Company and the other chemicals and reagents were from Merck. Deionized water was used in all of the experiments. The husks were provided by rice producers from Gilan.The surfactans were measured by using a Cecil Model CE9500 Uv-Vis Spectrophotometer. The particle sizes were determined by Fritsh Particle Size Analyzer. An optical microscope equipped with a camera was used for microscopic study of husks.

Measurement of surfactants

Concentration of anionic surfactants was measured using standard test method for Methylene Blue Active Substances [14]. The nonionic surfactants were measured according to standard methods for the examination of water and wastewater [15].

Optimization of Adsorption Parameters of Anionic Surfactants

The effect of pH on the ability of rice husks to adsorb surfactants was investigated. For this purpose, the pH of a 100 ml aqueous solution of 10mg/lit anionic surfactant was adjusted to 2, 3, 4, 5 and 6 using diluted H_2SO_4 and NaOH. 2gr husks were added to these solutions and they were stirred for 3 hrs. Then, the sample and standard solutions were filtered through a Whatman 43 filter paper.

The time dependency was also studied in a time period of 1, 2, 3, 4 and 5 hrs. The husk ash was also used for investigating the adsorption of anionic surfactants. For this purpose, the husks were totally burned in 750^0 C to give a white ash. 2gr of the ash was added to 100 ml of 10mg/lit anionic surfactant solution and adsorption was measured without changing pH and also in pH 2.

In a second method, a glass column with i.d. 2 cm was packed with 6gr of whole rice husk and compacted. 1 lit of a 10mg/lit anionic surfactant solution was passed through the column with the flow rate of 100 ml/min. Ten 100 ml fractions were gathered and the concentrations of remaining surfactant were determined. The same experiment was done with a column packed with milled husks having the particle sizes ranging from 30-40 meshes.

Optimization of Adsorption Parameters of Nonionic Surfactants

To study the effect of pH and time on the adsorption efficiency, the same procedure as mentioned above was repeated. The pH 8 and 10 were also investigated. Meanwhile, the adsorption of nonionic surfactant was investigated in a 100 ml aqueous solution of NPE with the concentration of 10, 20, 40 and 80mg/lit in the presence of 2gr husks.

The method using packed column was also applied. For this surfactant, the column was packed with 10gr of whole rice husks and 1 lit of 20mg/lit NPE solution was passed through the column with the flow rate of 200ml/min. The procedure was followed as the previous experiment for anionic surfactants.

Results and Discustion

Adsorption of anionic surfactants

The obtained results at different pH indicates that adsorption values increase in lower pH (figure 1), so that up to 93% of a 100 ml solution containing 1 mg of LABS was adsorbed by 2gr of husks. While, the adsorption value was less than 11% at pH 6 in the same condition.

Due to the weak basisity of LABS, its acidic form ($R-C_6H_4-SO_3H$) is predominant in acidic solutions (i.e. in the presence of H_3O^+) and better adsorbed by rice husk. For investigating in adsorption mechanism, we studied the effect of time on adsorption. In the flotation condition, the best adsorption value for LABS was obtained after 3hrs and at longer periods, desorption occurred. But, more amounts of AES were removed as the time increased. Figure 2 shows the time dependency of two anionic surfactants adsorption by rice husks in pH 4. Desorption of LABS is shown clearly in this pH. This finding allows concluding that LABS sorption from water is adsorption on rice husk particle surface, not biosorption. In the case of AES, we may suppose that the following hydrolysis occurs in acidic condition:

$$ROSO_3H \xrightarrow{H_2O} ROH + H_2SO_4$$

To investigate our assumption, the effect of concentration on adsorption values was studied. Figure 3 shows the adsorption values in the solution with 1, 10 and 100mg/lit concentrations after 1 and 5 hrs. The removal efficiency for the 100mg/lit solution was 56% after 5 hrs. It indicates that the adsorption capacity of 2gr rice husks is 5.6

mg from 10 mg of surfactant. In the more diluted solution (10 mg/lit), adsorption value is up to 80% after 5 hrs. Thus, the reaction does not proceed through hydrolysis, because the removal efficiency is dependent on concentration.

The adsorption values 600 ml of a 10mg/lit solution of LABS on a column containing 6gr rice husks is shown in table 1. The mean adsorption value was 75%. It seems that this method is more applicable for the removal of surfactants from wastewater and the desorption problem in longer periods is also solved.

It was thought that the fat body of husk might be related to the removal mechanism. Therefore, removal was examined using defatted rice husk. The result shows that the surfactant removal by rice husk cannot be attributed to the fat body of rice husks.

The obtained results with milled rice husks (30-40 mesh) show a 5% increase in adsorption efficiency, but it is not significant enough to be applied in industrial scale.

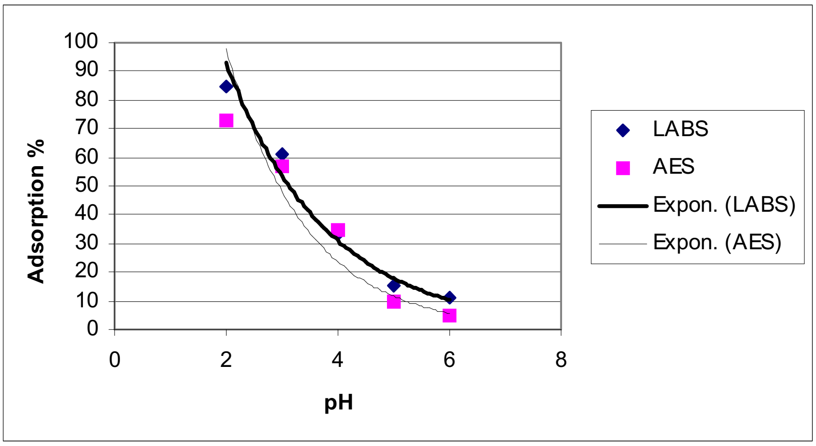

Figure 1. Effect of pH on adsorption of anionic surfactants. 2 grams rice husk in 100 ml solution with 10 mg/lit concentration and 3 hrs reaction time

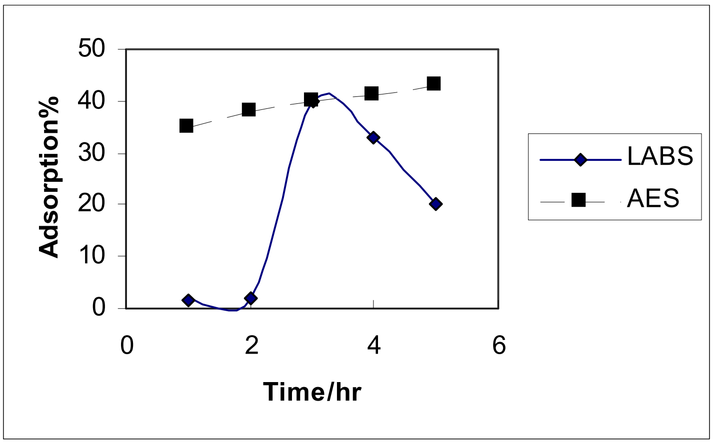

Figure 2. Effect of time on adsorption of anionic surfactants in pH 4, 2gr rice husk in 100 ml solution with 10mg/lit concentration.

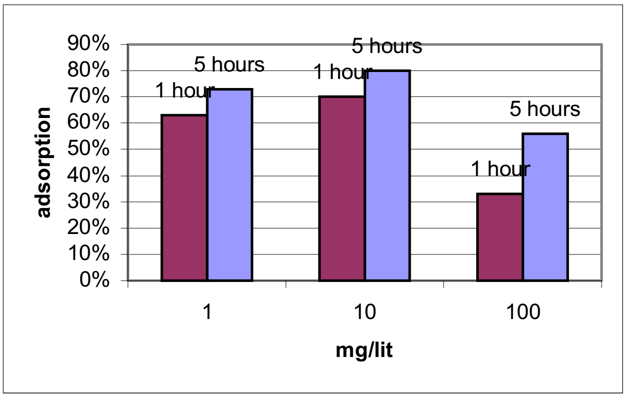

Figure 3. Adsorption values of a 100 ml AES solution with 1, 10 and 100 mg/lit concentrations in two stirring times and 2gr husks(pH 2)

Table1. The adsorption values of a 10mg/lit solution of LABS on a column containing 6gr rice husk (each fraction was 100ml)

Solvents	Adsorption values
First fraction	83%
2nd fraction	88%
3^{rd} fraction	78%
4^{th} fraction	79%
5^{th} fraction	68%
6^{th} fraction	52%

Adsorption of nonionic surfactants

There was no great difference in the adsorption values of NPE with the time changes. However, desorption was observed after 5 hrs, because its high solubility in water. Meanwhile, the pH changes were of no great importance in the adsorption amounts.

Table2. shows the adsorption values 100 ml of NPE solutions by 2gr husks. 2gr husks could adsorb 79% of 2mg NPE in 100ml solution (1.7mg). We expect to see at least the same result for a 40mg/lit solution of NPE. While the adsorption value was considerably decreased with an increase in the concentration and no adsorption was observed in the 80mg/lit solution. This may be related to micelle formation of nonionic surfactants. The critical micelle concentration (CMC) of NPE (with ethoxylation degree of 4-6) is variable between 0.0011-0.0044% (11-44mg/lit) [16]. Thus, in higher concentrations than 20mg/lit, the micelle formation is more probable. Addition of electrolyte for adjusting pH is another factor effective in CMC decrease. The obtained

results by using column showed that the adsorption yield is higher than floating method and adsorption value increases with decreasing the flow rate.

Conclusion

Our experiments on anionic surfactants revealed their low tendency to be adsorbed by husks in pH 6 and 7. While, more than 90% of these surfactants are adsorbed by husks in pH 2. The alkyl benzene sulfunates ($R-C_6H_4-SO_3Na$) are in sulfonic acid form under acidic condition. So they are adsorbed in their acidic form, not as ions.

Because of nonionic nature of nonyl phenol etoxylate, it does not require to change the pH for adsorption. The experiment results also show that the adsorption efficiency is limited and the husks surface is saturated with adsorbate. It seems that in all cases the sorption is via adsorption. Desorption during the longer times also confirm our assumption. Our finding on the adsorption of surfactants on husk ash showed that the ash is not responsible for adsorption process.

Fig. 4 shows the regular shape of husk ash in its microscopic image. The small pore sizes (<50μ) make them appropriate small cages to trap the molecules. If the surface tension is enough many molecules are easily trapped. Like the stationary phase in liquid chromatography (LC), the husk cellulose has coated the whole SiO_2 support and the fine support particles (with the mesh size of 300-400) improve the adsorption condition. Due to the long chains of surfactant, there is strong Van der Waals force between surfactants and cellulose chain, which provides a more desirable condition for adsorption.

The specific surface area of the husk ash powder was measured by BET method. It is 28-36 m^2/g, which is insignificant, compared to carbon active specific surface area (300-900m^2/g). Therefore, the specific area is not the unique factor in adsorption. But specifically, the distribution of cellulose layer on relatively large surface area of SiO_2 has considerably increased the adsorption efficiency.

Table 2. Adsorption values NPE in 100ml solution and 2gr husks in different concentration

Concentration (mg/lit)	10	20	40	80
Adsorption values (%)	50	70	22.5	0

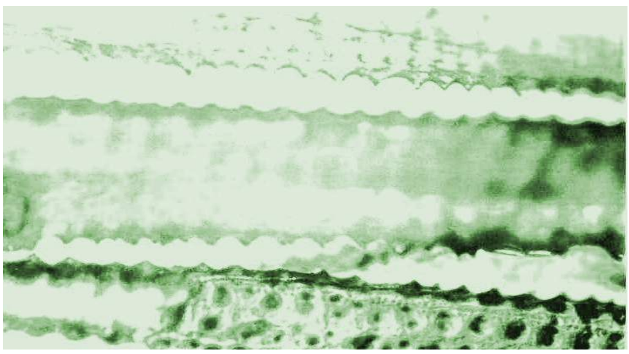

Figure 4. Microscopic image of husk ash

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