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Adsorptive Removal of Non-Ionic Surfactants from Water Using Granite Sand

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The adsorption of Triton X-100 in aqueous solution on the granite sand has been investigated to evaluate its ability as an adsorbent. Various parameters such as agitation time, adsorbent dose, adsorbent size, initial concentration of adsorbate, pH, temperature, and effect of interference ions were studied on the laboratory scale to establish optimum conditions for the removal of TX-100 from the effluents of different industries. Isotherm data were analyzed for possible agreement with the Langmuir and Frendlich adsorption isotherm equations. The first order rate equation by Lagergren was tested on the kinetic data. The rate of adsorption was conformed a pseudo first order kinetics with good correlation coefficient. The value of activation energy of sorption (E_a) was obtained as 44.6 kJ mol^{-1}. Results showed that granite sand exhibit reasonably good surfactant removals for non-ionic types. The possible role of the adsorbent in a chromatographic column was also worked out.

Keywords: Adsorption, TritonX-100, Granite sand, Langmuir and Freundlich isotherms, Adsorption kinetics

INTRODUCTION

The use of surfactants throughout the world is increasing at a rate in excess of the population growth because of generally improved living conditions and processed material availability in the less industrially developed countries of the third world. The ever-increasing demand of surfactant since the middle of this century is causing a great concern about its role in the environmental pollution. Surfactants cause foams at sewage treatment plants and pollute underground waters, which are hazardous for health. They exert a solubility effect on many organic compounds and create carcinogenic impacts, penetrated into water and change its quality by causing it to have an unpleasant smell and taste [1]. Surfactant removal from the industrial waste has been the subject of substantial research since the 1950s, when synthetic detergents came into a widespread use. An intensive data bases have been developed to support new commercial surfactant products for their safety and acceptability in the environment [2].

Some processes have been employed in order to solve the environmental problems caused by surfactants, including anaerobic and aerobic degradation [3], biodegradation [4,5], and adsorption technique [6-18]. Among these, adsorption is one of the effective methods available for such situations.

Much research has been conducted on the adsorption of ionic and non-ionic surfactants on coal [6,7], kaolin soil [8-10], lampblack [11], activated carbon [12], silica gel [13-15], clay [16] and rubber granul surfaces [17,18], etc.

The objective of this work was to develop a high performance and economical process for the treatments of non-ionic surfactants present in wastewaters through an adsorption process. Granite sand was used as a low-cost abundantly found adsorbing material. It is a coarse-grained, light colored, hard igneous rock consisting chiefly of quartz,

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orthoclase or microcline, and mica.

EXPERIMENTAL

Preparation of Adsorbent

Granite sand was purchased from the local market in a very cheap rate. The sand was first sieved to remove biggest particles and then washed several times with double distilled water, followed by settling and decanting. The residual solid was dried at 50 °C for 24 h.

Surfactant

Triton X-100 (a non-ionic surfactant) of AR grade was purchased from BDH Laboratory with 100% purity. The stock solution of TX-100 was prepared by dissolving in double distilled water.

Batch Adsorption Studies

In this study, surfactant adsorption characteristics of granite sand were investigated. The surfactant solution was added to the weighed sand (7.0 g) placed in a conical flask and shaked at a rate of 125 rpm with a mechanical shaker (VRN-360) for the predetermined contact period and filtered. The adsorbed amount of surfactant was obtained by measuring surface tensions of the solution before and after exposing with the adsorbent. A Stalagmometer (TRAUB'S Model: 4855) has been used for this purpose [19,20].

The surfactant concentration in the sorbent phase q (mg g^{-1}) was calculated from the following expression,

$$q = (C_o - C_f)\ V/m$$

where C_o and C_f are the initial and final concentrations (mg l^{-1}) of the adsorbate in solution, respectively, V is the volume of solution (l) and m is the mass of adsorbent (g).

RESULTS AND DISCUSSION

The effect of the dose of sand on the adsorption process is shown in Fig. 1. The plot between amount of adsorbent (g) and amount adsorbed (mg g^{-1}) indicates that the adsorption increases with an increase in the dose of sand. The maximum uptake is exhibited at 7.0 g of adsorbent.

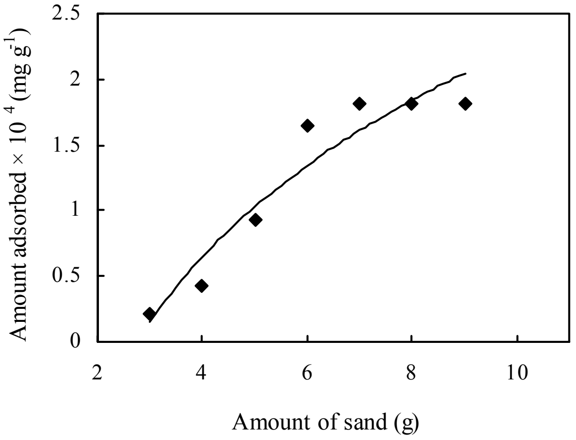

Fig. 1. Effect of the dose of adsorbent on the adsorption process. Conditions: surfactant concentration, 2 × 10 $^{-4}$ g l^{-1} ; temperature, 35 °C; pH, 5.74; agitation time, 15 min.

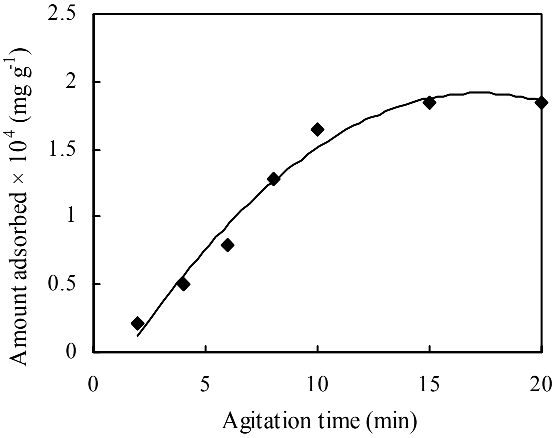

Fig. 2. Effect of agitation time on the adsorption process. Conditions: surfactant concentration, 2 × 10 $^{-4}$ g l^{-1}; temperature, 32 °C; pH, 5.74; amount of sand, 7.0 g.

The dependence of adsorption of TX-100 with agitation time is reported in Fig. 2. The adsorption increases with increasing agitation time and the equilibrium was attained after 15 min. Therefore, this time was set as agitation time for further work.

The work was also carried out by using granite sand of different particle sizes ranging from 300-1450 μm. Particle

Table 1. Effect of Adsorbent Size

No. of Sample	Size range (µm)	Amount adsorbed (mg $g^{-1} \times 10^4$)
S1	300-450	1.53
S2	475-700	0.95
S3	700-1000	0.91
S4	1000-1450	0.58

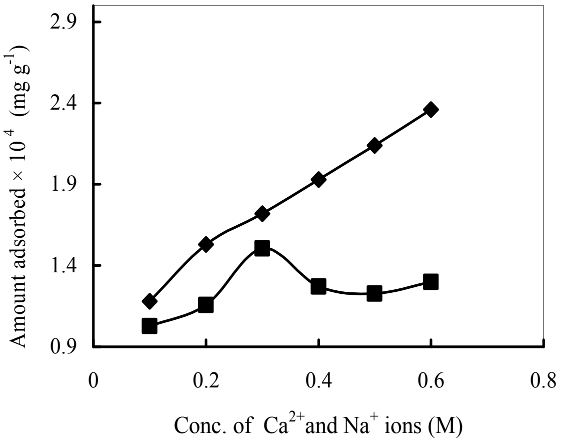

Fig. 3. Effect of Na^+ (■) and Ca^{2+} (•) ions on the adsorption process. Conditions: surfactant concentration, 2 × 10^{-4} g l^{-1}; temperature, 32 °C; pH, 5.74; amount of sand, 7.0 g.

size was examined by using a compound microscope (Cole-Parmer Model 48923-44). The removal of TX-100 decreased with an increase in the particle size, and maximum amount adsorbed (q) was observed on the finest particle size S1, due to largest surface area available (Table 1).

The presence of Na^+ and Ca^{2+} ions are very common in wastewaters. Therefore, the effect of the presence of both ions on the removal of TX-100 was investigated at a concentration range of 0.1-0.6 M (Fig. 3). The results showed that the higher concentration of Ca^{2+} ions provide a favorable condition in the removal of the non-ionic surfactant. However, as it is observed from Fig. 3, while the presence of increasing amount of sodium ions in a range of 0.1-0.3 M slightly increased the adsorption of surfactant, a further increase in the concentration (from 0.3 to 0.6 M) decreased the amount of adsorbed surfactant. This may be due to relative competition between sodium ion and surfactant species on the active center of granite, owing to the greater affinity of the Na^+ ions at higher concentrations.

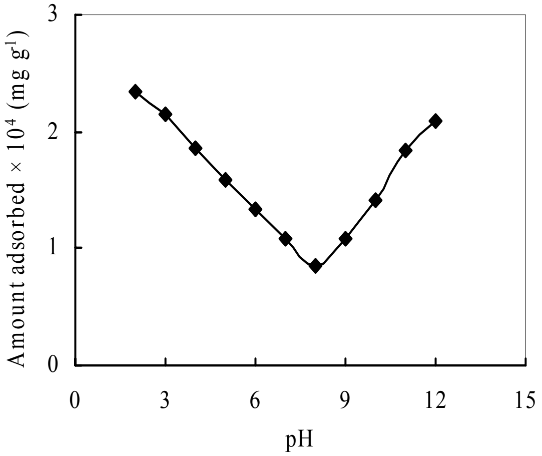

Fig. 4. Effect of pH on the adsorption process. Conditions: surfactant concentration, 2 × 10^{-4} g l^{-1} ; temperature, 34 °C; amount of sand, 7.0 g.

The pH of the aqueous solution is an important controlling parameter in the adsorption process and, thus, the role of hydrogen ion concentration was examined at different pH. The study was carried out in batch adsorption experiments over a pH range 2.0-12.0. The pH adjustment was done with the help of 0.1 M HCl or NaOH. The results given in Fig. 4 show that the adsorption capacity decreases with pH from 2.0 to 8.0, and increases with further increase in pH from 8.0 to 12.0. This conformed that the adsorption capacity of sand is highly pH dependent. It was observed that the addition of the nonionic surfactant changed the pH of the polluted water slightly acidic. Therefore, to achieve the actual conditions, adsorption studies were performed at pH 5.74.

The adsorption behavior of TX-100 onto granite sand at various temperatures is shown in Fig. 5. The adsorption capacity was going up by raising temperature, indicating that the adsorption interactions are endothermic. Similar results have already been reported in the literature [8].

Adsorption Model

The Langmuir and Freundlich models were used to

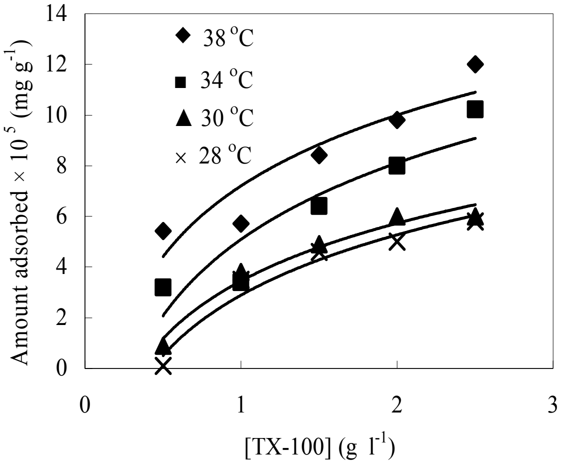

Fig. 5. Adsorption isotherms for Triton X-100 on granite sand. Conditions: pH, 5.75; amount of sand, 7.0 g; agitation time, 15 min.

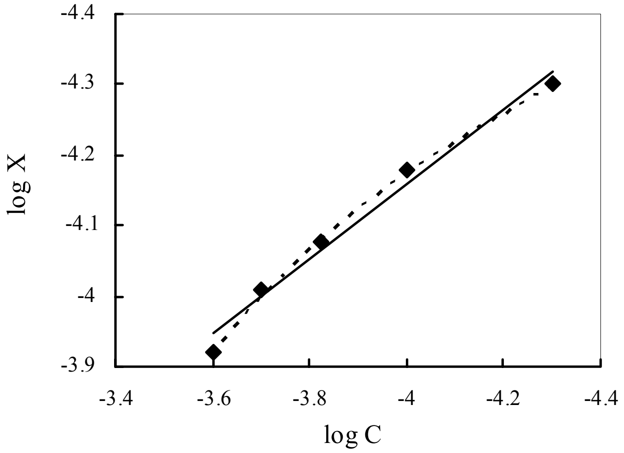

Fig. 6. Freundlich adsorption isotherm at 38 ± 0.5 °C.

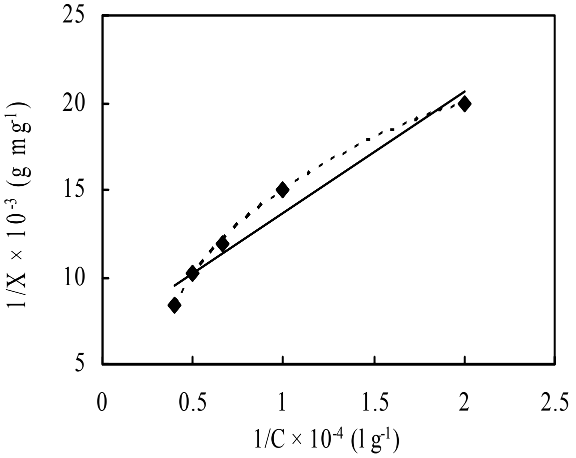

Fig. 7. Langmuir adsorption isotherm at 38 ± 0.5 °C.

Table 2. Constant Values from Langmuir and Freundlich Isotherms

Experimental Langmuir isotherm constants		Experimental Freundlich isotherm constants	
X_{max}	1.47×10^{-4} (mg g^{-1})	n	1.88
K	9.88×10^{2}	K	9.35×10^{-3}
r^a	0.9539	r^a	0.9805
r^b	0.9975	r^b	0.9983

[a] Correlation coefficient (linear regression). [b] Correlation coefficient (non- linear regression).

quantify the adsorption of TX-100 from aqueous solution onto the granite sand. Freundlich proposed the following model in 1907:

$$X = K [C]^{1/n}$$

A more convenient form of the above equation is:

$$\log X = \log K + 1/n \log C$$

where K and n are empirical constants, X is the amount adsorbed surfactant in mg g^{-1}, and C is the concentration of solute in the solution. Thus, a plot of logX *vs*. logC will yield a straight line (Fig. 6) with the slope 1/n and intercept of logK. It shows the validity of Freundlich isotherm.

According to Langmuir model (1918):

$$1/X = 1/X_m K \; 1/C + 1/X_m$$

where K is the constant of Langmuir adsorption, X_m is the limiting amount of adsorbate that can be taken up per mass of adsorbent, and C and X have the same meanings as in the Freundlich isotherm. A linear plot of 1/X *vs*. 1/C shows the applicability of Langmuir isotherm (Fig. 7). The correlation coefficient obtained with both kind of regressions (linear and non-linear) are shown in Table 2. Based on these parameters

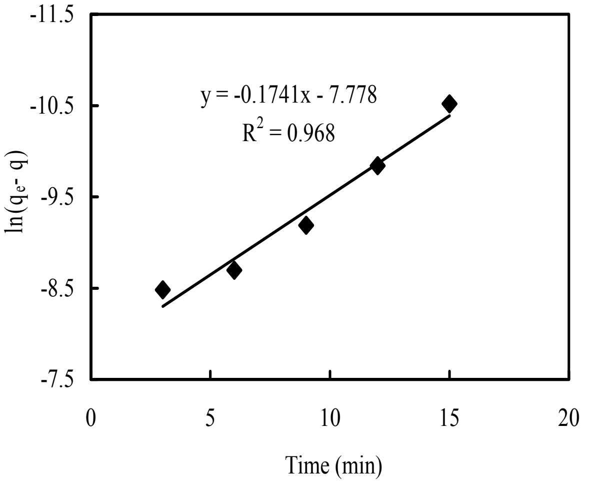

Fig. 8. Kinetic study of the adsorption process. Conditions: concentration of TX-100, 2.16×10^{-4} g l^{-1}; temperature, 32 °C; pH, 5.74; amount of sand, 7.0 g.

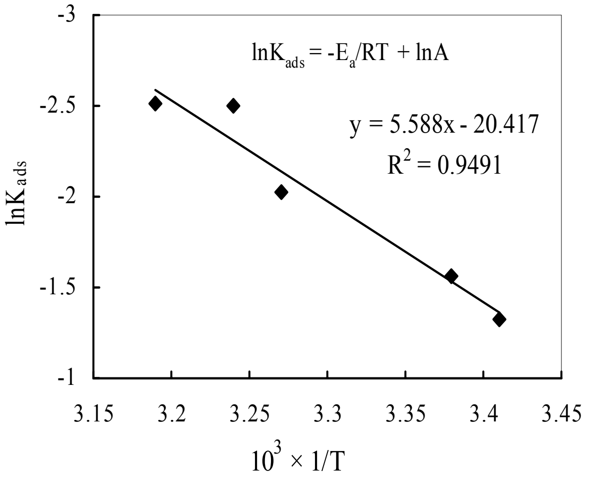

Fig. 9. Plot of $\ln K_{ads}$ against reciprocal temperature for TX-100 onto granite sand. Conditions: $C_o = 2.0 \times 10^{-4}$ g l^{-1}. pH = 5.75. Amount of sand = 7.0 g.

the data seem to be best fitted to the Freundlich model rather than the Langmuir model. However, the reverse situation was also reported [6,18].

Adsorption Dynamics

The rate constant k_{ads} is determined from the following first-order rate expression given by Lagergren (1898):

$$\ln(q_e - q) = \ln q_e - k_{ads}\, t$$

where q and q_e (mg g^{-1}) are the amounts adsorbed at time t (min) and at equilibrium respectively. A linear relationship was obtained by plotting $\ln(q_e - q)$ *vs*. time (Fig. 8). Similar results were reported in the adsorption of anionic and non-ionic surfactants on soil [8]. This plot proved that the adsorption process followed a pseudo first order kinetics. The rate constants are obtained by using the slope at different temperatures.

The adsorption rate constant is expressed as a solution function of temperature by the following relation ship.

$$\ln k_{ads} = \ln A - E_a/RT$$

where k_{ads} is the rate constant (min^{-1}), A is a temperature independent factor, E_a is the activation energy (kJ mol^{-1}), R is the gas constant (8.314 J mol^{-1} k^{-1}), and T is temperature (K).

For an increase in temperature from 293 to 313 K, the values

of rate constants were found to decrease from 0.264 to 0.081 min^{-1}. This observation agrees with the study on the sorption of acid dye with mixed adsorbents [21].

The $\ln k_{ads}$ values were plotted as a function of the reciprocal of the Kelvin temperature. A linear variation was observed (Fig. 9) with the following equation:

$$k_{ads} = 19.629\, e^{446/8314T}$$

where E_a (the activation energy of sorption) is equal to 44.6 kJ mol^{-1}.

Column Experiment

Recovery of the adsorbed material as well as the of column is also an important aspect of the practical application. For this purpose, dry granite sand was packed in a 20 cm long column having a 0.9 cm internal diameter, yielding an approximate packing density 1.49 g cm^{-3}. The column was slowly flooded with water and the surfactant solution was fed into the column from the top. The regeneration of the column was carried out by two ways: washing with the distilled water and washing with a 35% H_2O_2 solution.

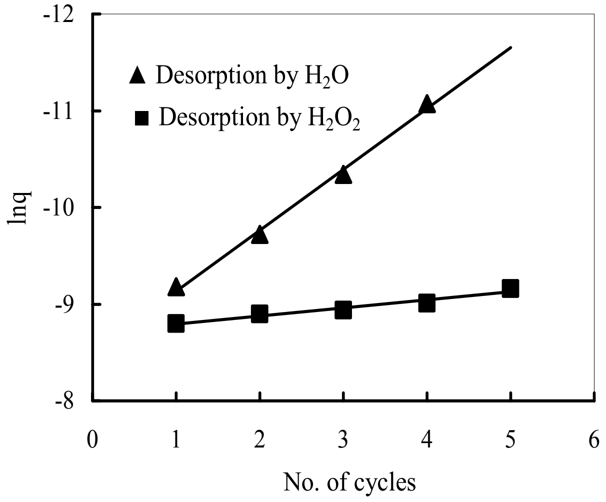

Fig. 10. Plots of lnq *vs*. number of cycles for the desorption processes by H_2O and H_2O_2.

The results revealed that, after four cycles, %adsorption decreased from 86.4% to 8.69% and from 85.5% to 63.9% by using H_2O and H_2O_2, respectively (Table 3). This infers that the column recovery with H_2O_2 solution is better than that with distilled water; therefore, the H_2O_2 solution was proved as a better desorbing agent. Figure 10 shows that the desorption processes follow a first order kinetics.

Test with Interference Ions

The utility of the adsorbent in column chromatography was tested by minor and trace metals. Composition and concentrations are given in Table 4.

In the presence of trace metal ions (*i.e.*, [b] Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+}) the adsorption capacity decreased because of the preferential adsorption of these metal ions onto the active centers of the adsorbent. However, the minor metals (*i.e.*, Na^+, Li^+, K^+, and Ca^{2+}) enhance the adsorption of surfactant by providing a suitable multilayer adsorption conditions for TX-

Table 3. Column Experiments for Regeneration of Column

No. of cycles	By H_2O		By 35% H_2O_2	
	Amount adsorbed (mg g^{-1} × 10^4)	Adsorbed (%)	Amount adsorbed (mg g^{-1} × 10^4)	Adsorbed (%)
Fresh adsorbent	1.540	86.40 ± 2.3	1.63	85.50 ± 3.7
1	1.025	57.47 ± 1.2	1.49	77.80 ± 2.4
2	0.599	33.59 ± 0.8	1.36	71.06 ± 2.3
3	0.321	18.03 ± 0.5	1.31	68.20 ± 2.1
4	0.155	08.69 ± 0.6	1.22	63.90 ± 0.8

Table 4. Effect of Interference Ions

Condition	Before ads. conc. of surfactant (g l^{-1})	After ads. conc. of surfactant. (g l^{-1})	Amount adsorbed (mg g^{-1})	Adsorption (%)
In the absence of interference ions	2.3×10^{-4}	0.333×10^{-4}	1.64	85.50 ± 2.7
In the presence of minor metal ions[a]	2.3×10^{-4}	0.153×10^{-4}	1.78	93.04 ± 3.5
In the presence of trace metal ions[b]	2.3×10^{-4}	0.819×10^{-4}	1.23	64.30 ± 1.9

[a] Na^+, Li^+, K^+, and Ca^{2+} = 100 mg l^{-1}. [b] Cu^{2+}, Cd^{2+}, Ni^{2+} and Pb^{2+} = 10 mg l^{-1}.

100. These results concluded that the granite sand can be used as an effective adsorbent for the removal of transition metals from the industrial effluents.

CONCLUSIONS

Many developing countries suffer from chemical contamination of water supplies, largely due to uncontrolled industrial activity. So, water treatment technique, which is able to deal with such pollutants in an effective way, is very valuable. The present study reveals that granite sand is an excellent adsorbent for surfactant removal from polluted waters. The proposed process is economically feasible and easy to carry out. Moreover, it can be used as an element in the household filter assembly.

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