Removal of Sulfur from Kerosene Oil by Adsorption on Plastic Clay

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The removal of mercaptan sulfur from kerosene-oil by adsorption on plastic clay at different temperatures has been studied. The extent of adsorption of sulfur from kerosene-oil on plastic clay increases from 87.0 to 94.0% with the increase of temperature from 303 to 323 K respectively. The Langmuir isotherm can be used to represent the equilibrium data at various temperatures. The process of adsorption is endothermic.

INTRODUCTION

Crude oil consists of various chemical impurities. Sulfur is recognised to be distributed throughout all fractions of crude oil. Sulfur compounds are undesirable in petroleum products because of their obnoxious odour, their potential corrosiveness and the reduction of the antiknock characteristic of tetraethyl lead by them. The sulfur in petroleum is present as hydrogen sulfide, free sulfur and organic sulfur compounds. The last one includes most of the sulfur in petroleum and mercaptans. The presence of mercaptans in crude oil and petroleum causes unpleasant laboratory and plant odours. The lower mercaptans are most malodorous. One part in 50 millions of ethanethiol can be detected in air by the human nose. At higher concentrations the odour changes to something like that of chloroform.

The common technique for the removal of sulfur from kerosene is the hydrodesulfurization which requires the use of a large quantity of molecular hydrogen for the catalytic extraction of organo-sulfurs from oil as hydrogen sulfide[1]. Obviously, this technique is costly and thus an economic process was in search[2,3]. In the present investigation the feasibility of using unconventional material, plastic clay, as an adsorbent for the desulfurization of kerosene oil has been studied.

EXPERIMENTAL

Plastic clay was obtained from Katni and Sihora mines (M.P.), India, and was used as such after passing it through 425 μm sieve. The chemical analysis of plastic clay was carried out using standard methods[4]. The analysis data are given in Table-1.

TABLE-1
CHEMICAL ANALYSIS OF PLASTIC CLAY

Constituents	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
% by weight	22.92	53.05	20.40	1.20	0.51	0.31

Organo-sulfur compound, 1-butanethiol (E. merck, AR) was used for preparing the solution in distilled kerosene oil with zero sulfur content. In order to measure the progress of adsorption the batch adsorption experiments were carried out by shaking 50 mL sulfur bearing solutions of different concentrations and temperatures in different glass bottles in a shaking thermostat; 5 g of plastic clay was used as adsorbent. The range of sulfur concentration varied from 250 mg/L to 1000 mg/L and the range of temperature studied was 303 K to 323 K.

The progress of adsorption was followed at different time intervals till the equilibrium was attained. The suspension was taken out at regular intervals, centrifuged and the supernatant liquids were analysed for sulfur content by silver nitrate method[5].

RESULTS AND DISCUSSION

Data reported in Table-2 shows that the amount of sulfur removal from the oil solution containing 250 mg/L of sulfur to the adsorbent increased from 2.175 mg/g (87% removal) to 2.35 mg/g (94% removal) with the increase in temperature from 303 to 323 K. The increase in the adsorption with the increase in temperature may be explained on the basis of increase in diffusion within the pores of plastic clay as diffusion is an endothermic process.

TABLE-2
TIME VARIATION OF ADSORPTION OF SULFUR ON PLASTIC CLAY AT DIFFERENT TEMPERATURES

Contact time (h)	Temperature					
	303 K		313 K		323 K	
	Amount adsorbed (mg/g)	% Adsorption	Amount adsorbed (mg/g)	% Adsorption	Amount adsorbed (mg/g)	% Adsorption
0.5	0.80	32.00	0.92	37.00	1.07	42.40
1.0	1.33	53.20	1.51	60.40	1.67	66.20
2.0	1.91	76.44	1.96	78.40	2.12	84.90
3.0	2.08	83.20	2.13	85.20	2.27	90.10
4.0	2.14	85.80	2.18	87.48	2.32	92.80
4.5	2.17	87.00	2.21	88.60	2.35	94.00
5.0	2.17	87.00	2.21	88.60	2.35	94.00
6.0	2.17	87.00	2.21	88.60	2.35	94.00

The rates of adsorption of mercaptan sulfur from kerosene oil to plastic clay at different temperatures were calculated by the Lagergen equation:

$$\log (q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t$$

where q_e and q are amounts of sulfur adsorbed at equilibrium at any time t and K_{ad} is the rate constant.

The rate constants were calculated from the slopes of Lagergen plots (Fig. 1) and found to be 7.7×10^{-3}, 7.94×10^{-3} and 8×10^{-3}/h at 303, 313 and 323 K respectively at the concentration of 250 mg/L of sulfur in oil. The increase in rate constant for adsorption with the increase in temperature of solution showed the endothermic nature of adsorption.

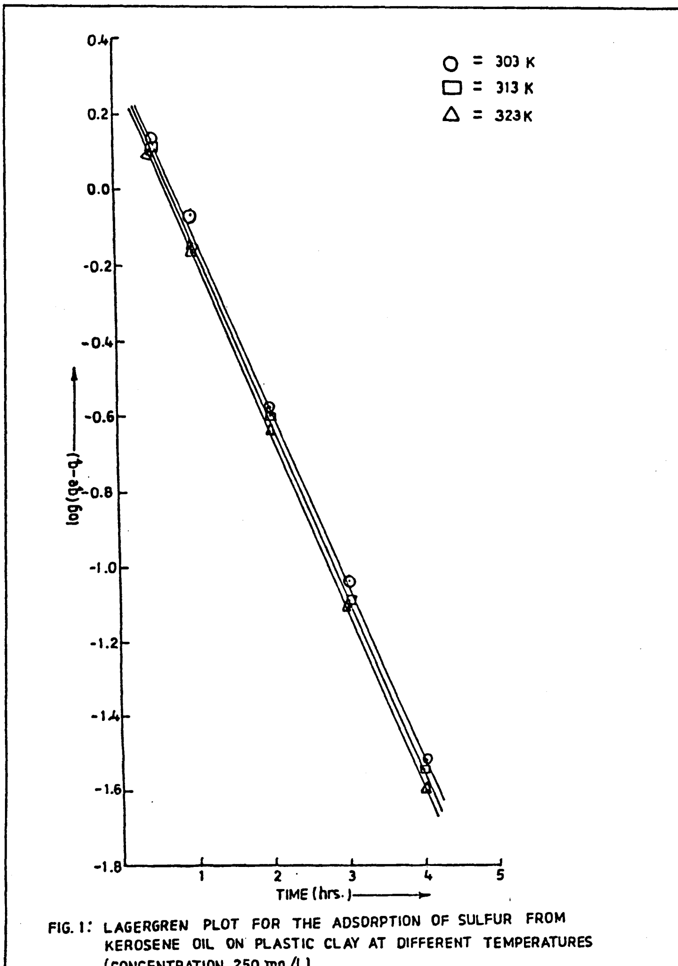

Fig. 1 Lagergen plot for the adsorption of sulfur from kerosene oil on plastic clay at different temperatures (concentration 250 mg/L).

Adsorption isotherm

The rearranged Langmuir equation used to study the equilibrium nature of the adsorption of sulfur on plastic clay at different temperatures could be written as

$$\frac{C_e}{q_e} = \frac{K}{Q_0} + \frac{C_e}{Q_0}$$

where K and Q_0 can be related to the equilibrium constant and to sorption maxima respectively. C_e and q_e are equilibrium concentration and amount adsorbed of adsorbate at equilibrium. The linear plots of C_e/q_e *vs.* C_e confirm the validity of Langmuir model for this process. The values of Langmuir constants Q_0 and K were determined (Table-3) from the slopes and intercepts of linear plots of C_e/q_e *vs.* C_e at different temperatures.

TABLE-3
LANGMUIR CONSTANTS AT DIFFERENT TEMPERATURES

Temperature K	Q_0 (mg/g)	K (mg/L)
303	2.50	3.75
313	2.82	4.23
323	4.03	6.05

This study showed that naturally occurring low cost plastic clay can be used as an effective adsorbent for sulfur removal.

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(*Received*: 4 January 1999; *Accepted*: 3 April 1999) AJC-1709