ADSORPTION OF OIL-GREASE FROM OIL-IN WATER DISPERSIONS ON DIFFERENT THERMAL ACTIVATED CLAY MINERALS

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ABSTRACT

Thermal activated clay minerals like montmorillanite, illite, muscovite and kaolinite were investigated to determine their adsorption capacity for removal of oil-grease from synthetically prepared oily water by batch adsorption. The clay samples used in this study were supplied from Marmara (used for ceramic industry) and Mediterranean regions in Turkey. In experimental studies, optimum values of pH, contact time, dosage of clays and particle size of the adsorbent were used. Natural clay samples were heated from 110 °C to 900 °C for 1 hour to obtain thermal activated clay samples. The oil retained after the adsorption is determined by UV spectrum of oil. In this method, percentage removals of oil-in water dispersions were observed from 78 to 94 %. The maximum adsorption capacity of oil-grease was accomplished when the illite clay was used. The order of adsorption capacity of oil-grease was illite > kaolinite ~ montmorillanite > muscovite. It was observed that the adsorption capacity decreases with increasing temperature.

Keywords: Adsorption, Oil-grease, Thermal activated clay.

INTRODUCTION

Oil-grease effluent is produced in municipal sewers, petroleum refineries, petrochemical plants, steel mills, workshops, food processing plants, and in

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the textile industry.

Oil-grease must be removed from wastewater since these materials interfere with other processes (particularly gravity settling) and may accumulate in unwanted areas of the treatment system causing a performance problem. Furthermore, if oil-grease passes through to a receiving body of water, it composes an oil layer and this layer causes a significant pollution problem in the form of reduced light penetration and photosynthesis. Also it hinders oxygen transfer from atmosphere to water medium. As a consequence the amount of dissolved oxygen in the bottom layer of water will be decreased. This situation affects survival of aquatic life in water. The removal of oil-grease from wastewater can be accomplished by the use of several well-known and widely accepted techniques. Conventionally, gravity separation, dissolved air flotation, chemical coagulation, filtration, membrane processes, biological processes, adsorption are used for the removal of oil-grease /1.2/.

Adsorption techniques have been successful in removing oil-grease. Clay minerals have been the most widely used absorbent because its cost is low and they can be reached easily. Oil-grease adsorption on various sorbents has been studied by many researchers /3-31/.

MATERIALS AND METHODS

The clay samples used in this study were supplied from Marmara and Mediterranean regions [Muscovite (Beykoz, İstanbul); Kaolinite (Şile, İstanbul); Illite (Çanakkale) - These clay samples are used in the ceramic industry-; Montmorillanite (Elbistan, Kahramanmaraş)]. The four clay samples were air dried and sieved from 425 μm sieve. Chemical composition of the clay samples were determined by X-ray diffraction. The results are given in Table 1.

Properties of the selected clay samples were determined by X-Ray-Fluorescence spectrometry. The results are given in Table 2. According to XRF results, the component in maximum amount inside of clay has been accepted as basic mineral of clay.

Surface area measurements of natural and thermal activated clay minerals were made and the results are given in Table 3.

Table 1.
Chemical composition of clay samples

Type of clay mineral	% Moisture	% Weight of loss	Constituent and Percentage Present								
			SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
Muscovite	4.64	14.15	47.13	23.61	11.01	1.26	0.29	1.09	2.34	0.06	0.12
Kaolinite	2.03	9.70	61.18	22.93	2.27	1.13	0.08	0.46	2.10	0.04	0.11
İllite	2.29	10.07	57.13	23.61	4.02	1.04	0.14	0.60	2.74	0.04	0.10
Montmorillanite	11.30	23.62	49.12	16.84	6.95	0.69	2.44	2.02	1.55	0.02	0.05

Table 2.

Mineral content of clay samples

Sample	Mineral Content (%)	
Muscovite	Quartz	37.95
	Kaolinite	9.65
	Kaolinite-Montmorillanite	5.02
	Muscovite-1L-Magnesion	39.83
Kaolinite	Quartz	62.96
	Muscovite	11.40
	Montmorillanite	11.50
	Kaolinite	14.14
İllite	Quartz	66.91
	Illite	17.98
	Kaolinite	11.39
	Montmorillanite	3.73
Montmorillanite	Quartz	8.95
	Illite- Montmorillanite	14.45
	Montmorillanite	49.00
	Muscovite	27.61

Table 3.

Surface areas of clay samples*

Sample	Type of clay minerals	Surface area (m^2/g)
Muscovite	N	65.0
	TA (110 ^{0}C)	61.0
	TA (850 ^{0}C)	45.0
Kaolinite	N	25.0
	TA (110 ^{0}C)	19.6
	TA (900 ^{0}C)	120
Illite	N	30.0
	TA (110 ^{0}C)	24.5
	TA (900 ^{0}C)	21.0
Montmorillanite	N	201.0
	TA (110 ^{0}C)	194.0
	TA (700 ^{0}C)	142.0

*N: Natural clay sample; TA: Thermal activated clay sample

EXPERIMENTAL

Natural clay samples were heated from 110 °C to 900 °C for 1 hour to obtain thermal activated clay samples. Then samples were put in a desicator containing dried silicagel. Adsorption experiments were carried out in a cylindrical vessel (2.4 L). The constant initial concentrations of 800-920 mg/L of engine oil (SAE 40) were dispersed in 250 mL drinking water by stirring for 5 minutes (synthetically wastewater). Mixing was provided by a stainless-steel stirrer while maintaining the stirring speed at around 1400 rpm. Then the clay sample of 5 g (optimum amount of clay) was added into this mixture and stirred again for 12 minutes (optimum contact time). At the end of adsorption period, the supernatant was centrifuged for 10 minutes at 2000 rpm. The concentration of oil-grease in the supernatant solution was determined by using UV spectrophotometer. The supernatant solution (acidify with HCl to pH 1) was extracted with 30 mL (three times) of trichloroethylene (Merck 958) separatory funnel. The oil content of investigated oil-in water dispersions was completely removed by using trichloroethylene extractions. Residual concentration of engine oil was calculated with the help of a calibration plot obtained by measuring the absorbance at 274 nm. The amount of adsorbed oil was calculated with the help of the following mass balance equation:

$$\text{Amount of adsorbed oil } (\text{mgg}^{-1}) = [(Co-Ce)/m].V,$$

where Co and Ce are the initial and equilibrium concentrations (mgml^{-1}) of oil solution, respectively, V is volume of oil-in water dispersions (mL) and m the amount of adsorbent in gram.

RESULTS AND DISCUSSION

The results of experiments on the four activated clay samples are given in Fig 1.

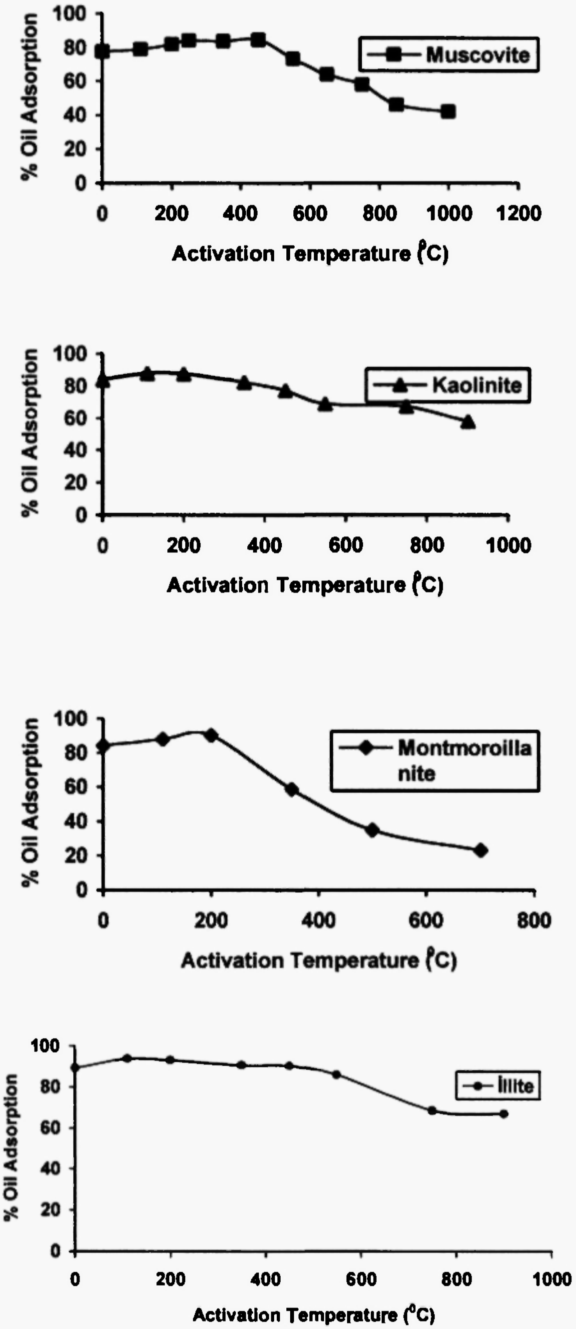

Fig. 1: Effect of temperature on percentage adsorption of oil at natural and thermal activated clay minerals.

As seen in Figure 1, the adsorption capacity of muscovite is increased with temperatures up to 500 °C and decreased at higher temperatures. The adsorption capacity of thermal activated muscovite at about 250 °C is 7-8 % more than natural clay sample of muscovite.

By the activation of kaolinite, its adsorption capacity is increased as 4,5 %. The decrease in adsorption capacity of kaolinite with the increasing temperature is as slow as muscovite. However, the decrease in adsorption capacity of kaolinite (at about 400 °C) is started at lower temperature than muscovite (at about 500 °C), because the montmorillanite content of kaolinite is more than that of muscovite, respectively 11,5 % and 5,02 %.

The adsorption capacity of thermal activated illite is increased as 5,5 % according to natural illite mineral. It is seen that there is no significant loss of adsorption capacity of illite at about 550 °C. The reason for this is that the clay sample has a smaller amount of montmorillanite than other clay samples, 3,73 %. The capacity of oil-grease adsorption is decreased with temperatures higher than 600 °C.

The adsorption capacity of montmorillanite is increased as 7,0 % by activation; however, it started to decrease rapidly at about 200 °C. The reason for the rapid decrease is high montmorillanite content of this clay sample, 49,0 %.

CONCLUSION

In this study, adsorption of oil on different thermally activated clay samples is investigated. Oil-grease adsorption and optimum thermal activation temperature of clays are decreased by increasing amaount of montmorillanite inside the clays. Because of the montmorillanitic clays have high amount of moisture and are decomposited easily with heat.

According to experimental studies, the oil-grease adsorption capacity of muscovite, which comprises montmorillanite in an amount of 5,02 %, increases up to 500 °C. The montmorillanite content of kaolinite is 11,5 %. A decrease in oil-grease adsorption is seen at temperatures higher than 350 °C. The clay which has an amount of montmorillanite of 49 % shows an enormous decrease in the oil-grease adsorption at temperatures higher than 200 °C.

The thermally activated clay samples from 300 °C to 900 ° C show a general decrease in the surface area values, which may be due to closed micropores as the temperature increases. The thermally activated clay samples from 100 °C to 300 °C show an increase because of the removal of water hanging on the micropores, thus preventing the oil-grease adsorption.

The order of removal of oil-grease from the test solution by thermally activated clays is thus: illite > montmorillanite > kaolinite > muscovite.

The surface areas of thermally activated clays have been determined and the results have been given in Table 3. From the results of the experiments, it is observed that the adsorption capacity not only depends on the surface area of natural or thermal activated clays but also the chemical structure of adsorbent material. This study indicated that the thermal activated clay samples such as muscovite, kaolinite, montmorillanite and illite can be used for oil in water dispersions. The efficiency of oil removal is obtained to be 78-94 %.

In conclusion, it can be said that the present thermal activated clays can be used as effective, low-cost adsorbents for the removal of oil-in water dispersions and it is observed that the adsorption capacity decreases with increasing temperature.

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