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# Investigation of gas oil separation from wastewater using a specific natural clay as adsorbent

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## ABSTRACT

In this study separation of gasoil from wastewater has been investigated by using three types of natural clays (NCs) and two commercial organoclays, cloisite 15A, and cloisite 30B. Initial results of gas oil adsorption by these clays showed that one of the NCs was much more attractive than the others because of its much better adsorption performance as well as its low cost and availability. This clay was called super adsorbent clay (SAC). Three NCs were characterized by X-ray diffraction (XRD), and it was shown that SAC mainly contains lead oxide. Adsorption performance of SAC was obtained at various temperatures (20–60°C), pHs (3–12), mixing times (2.5–30 min), mixing rates (50–600 rpm), and different amounts of clay (0.1–1 g). It was found that mixing time and rate of mixing were much more important factors. Isotherm models were applied for the system and it was found that the Freundlich isotherm can predict the adsorption of gasoil onto SAC more accurately, especially at higher concentrations. Finally, regeneration of gasoil-saturated SAC was studied at different temperatures. Results showed that saturated SAC can be regenerated completely at a temperature of 180 °C and at a time period of about 8 min.

*Keywords:* Gasoil removal; Adsorption; Natural clay; Wastewater treatment

## 1. Introduction

At present, water pollution is a global problem that has excited more public concern than any other wastes, especially for regions with limited sources of water. Water pollution is deterioration of the quality of water mainly due to admission of oil, oil products and extrinsic chemical materials [1].

Gas oil is one of the most important energy carriers all over the world. Common gasoil is composed of about 75% saturated hydrocarbons (primarily paraffins including normal, iso, and cycloparaffins), and 25% cyclic hydrocarbons (including naphthalenes and alkyl benzenes). The average chemical formula for common gasoil is $C_{12}H_{23}$, ranging from approximately $C_{10}H_{20}$ to $C_{15}H_{28}$ [2].

A risk of spillage of gas oil exists when it is transported, stored in storage tanks, and even when it is used. Because of its relatively high boiling range, gasoil spilled on a road will stay there until it is washed away by sufficiently heavy rain, whereas lower boiling range fuels such as gasoline will quickly

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evaporate. A portion of the light fractions will evaporate, and the remaining gasoil will make a greasy slick on the road that can destabilize moving vehicles. This greasy slick severely reduces tire grip and is responsible for many car accidents.

Gas oil pollution of water sources (sea, rivers, underground sources, etc.,) has steadily increased with the increase in gasoil consumption that has significant environmental impact [3]. Gasoil pollution of shore, in addition to the reduction of amenity, also affects marine and shore life and vegetation [4].

Gas oil and other products of crude oil spilled in water undergo physicochemical changes such as evaporation, dissolution, photo-oxidation, dispersion, microbial degradation, and spreading [5]. Previous studies show that some of these physicochemical changes, especially photo-oxidation of gas oil in the aquatic environment leads to the formation of harmful products such as aromatic, aliphatic, benzoic, and naphthenic acids. The most toxic effects are caused by aromatic components because aromatics are known to be more recalcitrant [6–8].

Numerous methods have been applied for wastewater treatment including mechanical, physicochemical, chemical, and biochemical processes. Some well-known technologies have been used for gas oil removal from water such as chemical treatment, gas floatation, granular media filtration, cartridge filtration, and adsorption [9]. While some advanced methods can be applied in oily water treatment such as ultra membranes and membrane bioreactor, the expensive initial costs usually prohibit wider applications [10]. Among the mentioned techniques, adsorption is popular because it is cheap, simple, and effective [3].

Activated carbon has been one of the most common adsorbents for wastewater treatment. Carbon active is effective for removing a wide range of organic molecules from water; however, its adsorption efficiency is very low for gasoil due to the fact that emulsified gasoil can blind its pores [11].

Among the various adsorbents, some natural clays (NCs) are good choices for hydrocarbon removal from wastewater. However, many NCs are ineffective for adsorbing nonpolar and nonionic organic compounds (NOCs). The inorganic exchange cations of many NCs (i.e. $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$) are strongly hydrated in water [12]. To overcome this problem, inorganic exchange cations were replaced with organic cations of the form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NR_2]^+$, where R is a large ($C_{12}$ or greater) alkyl hydrocarbon [13]. The organic alkyl groups reside in the interlayer region of the clay structure and remove NOCs from water.

It was found in some studies that NOCs adsorption increased as the organic-cation molecular weight and clay-layer charge were increased [14,15]. It was also shown that bentonite organoclay was quite effective for removing oil from a number of oil-in-water emulsions [16]. Beall [17] applied organoclays in combination with activated carbon and reverse osmosis to treat wastewaters contaminated with organic pollutants. He found that organoclays have a synergistic effect with activated carbon and other unit processes such as reverse osmosis. Mysore et al. [18] showed that the hydrocarbon sorption capacity of the organoclays depends significantly on the materials and surfactants used in the modification process. De Oliveira Pereira et al. [19] measured the toluene, diesel fuel, and gasoline sorption capacity of clay modified with a quaternary ammonium salt. They showed that their organoclay adsorbed more gasoline and toluene than diesel and kerosene. Salehi et al. [20] studied two commercial organoclays (Cloisite 15A and Cloisite 30B) for removal of light and heavy crude oils from salty waters. They found that the oil removal efficiency for Cloisite 30B is higher than that of Cloisite 15A and the greater sorption was observed for Gachsaran crude oil (95.9–97.5%) onto the organoclays over Soroosh crude oil (92–95.6%).

High-adsorption performance, availability and relatively low price of some NCs or modified organic clays make them very interesting for the treatment of oily polluted wastewater. The main problem of applying NCs is to find a very active one to have necessary specifications of a powerful adsorbent. Therefore, further investigation is required to find active NCs or to modify organic clays to reach higher adsorption efficiencies.

In this research, an experimental analysis was performed to adsorb gasoil by three types of NCs, and two commercial organoclays. None of the used NCs were previously used for treatment of oily waters; however, they were selected based on their similar applications in other industries, their cost and availability. For instance, one of them, found to be a very active adsorbent (called super adsorbent clay, SAC), is traditionally used as an antiperspirant and antiodorant in some parts of Iran. It is also extensively applied in manufacturing of lead glass and ceramic glazes as well as in fine dinnerware. Other less dominating applications include the vulcanization of rubber and the production of certain pigments and paints. The efficiency of those NCs was checked for gas,oil adsorption and the best one (SAC) was selected for more detailed studies. Three NCs were characterized by powder X-ray diffraction (XRD), and XRD patterns were analyzed by X'pert high score software to identity important species that were effective for gas oil adsorption. Isotherms of gasoil adsorption by SAC were obtained at different temperatures, pHs, mixing times, rates of mixing, and dosage of SAC. Finally, the regeneration of gas oil-saturated SAC was studied at four different temperatures.

## 2. Experimental

### 2.1. Materials and equipment

Three types of NCs (Fig. 1) were obtained from mines of Shiraz, Iran. In Fig. 1: 'A' refers to SAC and 'B' and 'C' are two other NCs. Two commercial organoclays, Cloisite 15A and Cloisite 30B (Fig. 2) were supplied from Southern Clay Products Incorporation (Texas, USA). In Fig. 2 'A' refers to cloisite 30B and 'B' is cloisite 15A. The spacing of each NC-smectite was examined using XRD (model rad A, Rigaku, Tokyo, Japan). Gas oil was prepared from one of the gas oil stations in Shiraz, Iran (density 0.87 g/mL, average molar weight 250, sulfur content about 500 ppm). A pH meter (model HAch Sension 1, portable, Colorado, USA) was used to control pH of solutions. All other chemicals used in this study (N-Hexane, NaOH, HCl and etc.) were obtained from Merck (Darmstadt, Germany).

### 2.2. Adsorption experiment methods

Each sample of gas oil in water was emulsified to a specified amount of 1,000 ppm of gas oil in 50 mL of water. A mechanical mixer was used for 15 min to ensure a good mixing of gas oil and water. Then, each sample of clay was placed in the emulsion until the equilibrium was reached. After which, saturated clays were separated by Watman No. 42 filter paper (Kent, UK). The remaining gas oil in water was extracted by 50 mL n-hexane in two stages and gas oil content was measured by using UV spectrophotometer at wavelength of 246 nm (Genesys 10 UV, Thermo Fisher Scientific, Madison, USA). The adsorption capacity of each clay was measured by comparison of its weight before and after adsorbing gas oil.

Fig. 2. Two commercial organoclays, A: Cloisite 30B, B: Cloisite 15A.

### 2.3. Regeneration procedure

NCs saturated with gas oil were used to investigate the regeneration performance. For this purpose, each saturated sample was placed in a beaker and the beaker was heated to a specified temperature. The sample was heated for 10 min, and the change in beaker weight was recorded each one minute. This procedure was applied for several temperatures to find the best condition for regeneration of saturated clays.

## 3. Results and discussion

### 3.1. Adsorption performance of clays

Gas oil removal was measured in different weights of fresh clays as adsorbent from 0.1 g until 1 g. Initial gas oil content was 1,000 ppm in 50 mL of water for all experiments at temperature 25°C and pH = 7. Each sample was mixed for 30 min at a mixing rate of 600 rpm, and then the final gasoil concentration in water was measured. Figs. 3 and 4 compare the adsorption performance of these clays. Fig. 3 shows that the remaining gasoil in water (not-adsorbed gas

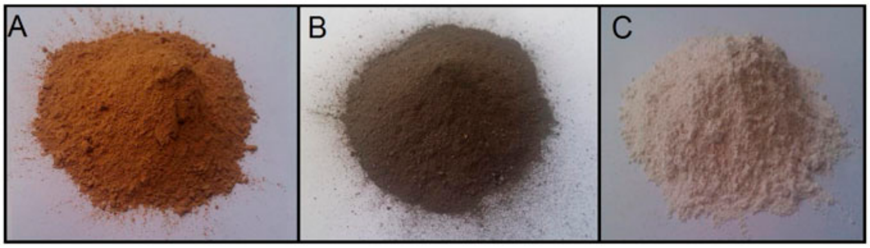

Fig. 1. Three types of NCs; A: SAC; B and C: two other NCs.

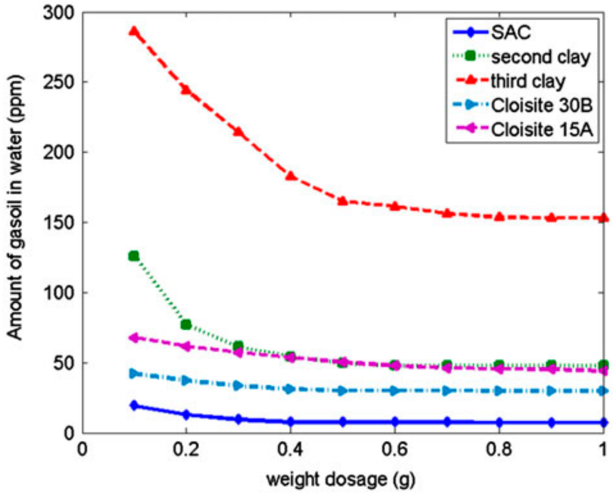

Fig. 3. Gasoil adsorption by three types of NCs and two commercial organoclays ($T = 25\,^\circ C$, pH = 7, 30 min mixing by rate 600 rpm).

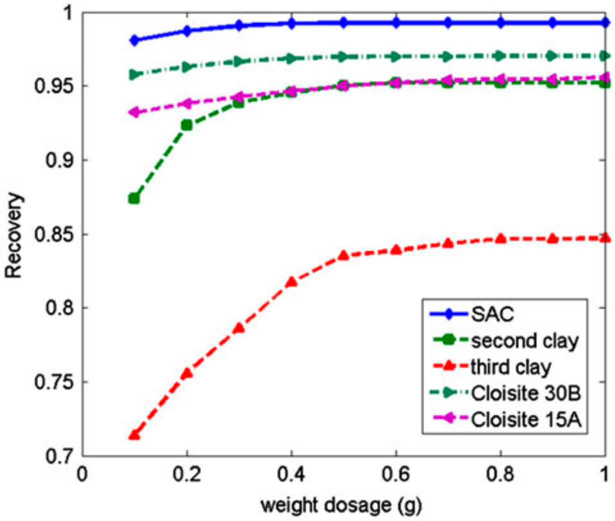

Fig. 4. Gasoil recovery by three types of NCs and two commercial organoclays ($T = 25\,^\circ C$, pH = 7, 30 min mixing by rate 600 rpm).

oil) for super natural clay is much lower than those of other clays. Surprisingly, this clay can reduce gasoil content of polluted water from 1,000 ppm to lower than 10 ppm. Another advantage of SAC is that this clay is a very active adsorbent, even in low weight dosages, while the adsorption performances of other NCs reduce significantly in lower weight dosages.

Fig. 4 reveals that the adsorption recovery of SAC is considerably high (98–99.5%) for all weight dosages. The recovery of second natural clay can reach to about 95% only by applying a high amount of clay, while the recovery of third natural clay is maximum 85%. These two figures clearly show that SAC is a very active adsorbent compared with other natural and organic clays, and thus, this clay was selected for more detailed studies and its results will be discussed in the following sections.

### 3.2. XRD analysis of NCs

The XRD patterns of three NCs have been shown separately in Fig. 5(a)–(c). These XRD patterns have been analyzed by X'pert high score software for chemical analysis. It was found from Fig. 5(a) that SAC mainly contains PbO, which is one of the reason for the very good adsorption performance of this clay. Second clay mainly contains $SiO_2$ and $CuFeS_2$ (Fig. 5 (b)), while the third clay contains $CaCO_3$, and a small amount of $SiO_2$ (Fig. 5(c)). Therefore, the main active adsorbent in second and third NCs is $SiO_2$. The low adsorption capacity of the third natural clay can be attributed to the high amount of $CaCO_3$ in this clay.

### 3.3. Effects of mixing time

The effect of mixing time on the adsorption of gas oil has been investigated at various mixing times from 2.5 to 30 min. Initial gas oil content was 1,000 ppm in 50 mL of water at 25 °C and pH = 7 for 1 g of SAC and at a mixing rate of 600 rpm. As it is seen from Fig. 6, mixing time has significant effect at small mixing times; however, equilibrium was reached relatively fast at a time around 10 min. It means that SAC has a fast mixing time as well as its high adsorption capacity, which are necessary conditions for industrialization.

### 3.4. Effects of temperature

The effects of temperature on the adsorption of gas oil have been shown in Fig. 7. The temperature range of 20–60°C has been studied for 1,000 ppm of gas oil in 50 mL of water. SAC was used as adsorbent for a mixing time of 30 min and the other conditions are the same as Section 3.3. This figure shows that the adsorption of gas oil by SAC decreases as the temperature is increased. By changing the temperature from 20 to 60 °C, the amount of gasoil adsorption does not change significantly (6–15 ppm) and the amount of recovery decreases from 99.4 to about 98.5%. This degree of recovery reduction might not be important in some conditions and for some practical applications, because it should be considered that each change in temperature needs a certain level of energy and cost that may not be practical at industrial scales.

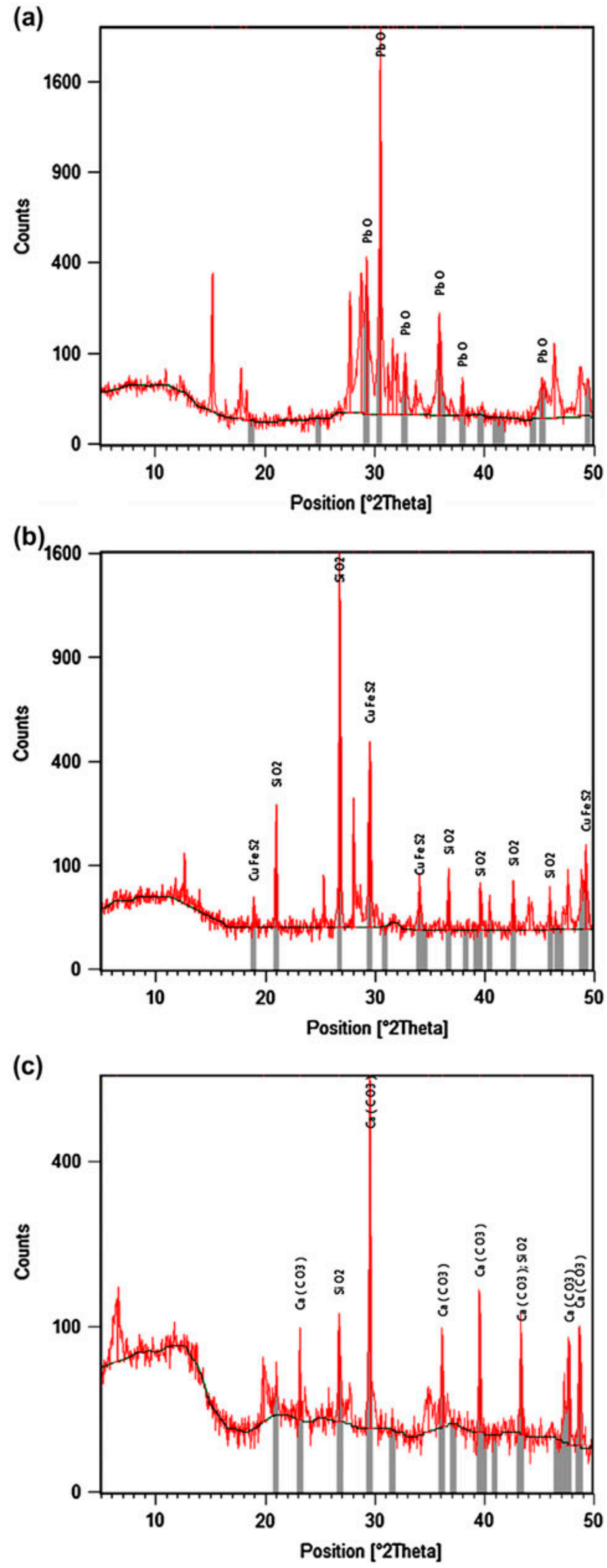

Fig. 5. (a): XRD patterns of the first natural clay (SAC), (b): Second natural clay, (c): Third natural clay.

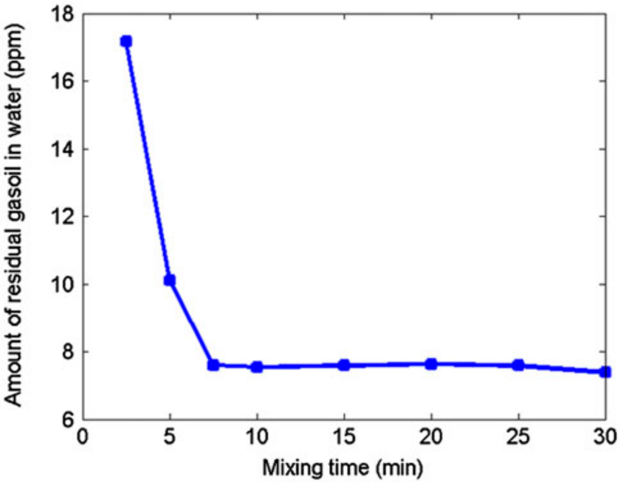

Fig. 6. Effects of mixing time on the adsorption of gasoil (1 g of NNC, $T = 25\,^\circ C$, pH = 7, initial gasoil content = 1,000 mg/L in 50 mL water).

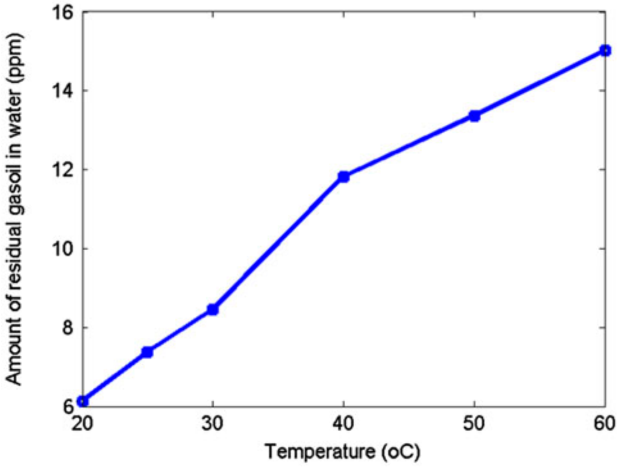

Fig. 7. Effects of temperature on the adsorption of gasoil (1 g of SAC, pH = 7, initial gasoil content = 1,000 mg/L in 50 mL water, 30 min mixing).

The effects of higher temperatures on the adsorption performance of SAC will be discussed in the regeneration section.

### 3.5. Effects of pH

Acidity (pH) is usually an important parameter affecting the adsorption of pollutants on the adsorbent surface [17]. The effects of pH on the adsorption performance of SAC were investigated in the range of pH 3–12 for 1,000 ppm of gas oil in 50 mL water. The other conditions are the same as Section 3.3. Fig. 8 reveals that by increasing pH from 3 to 12 the amount of residual gasoil in water is decreased from 11.3 to

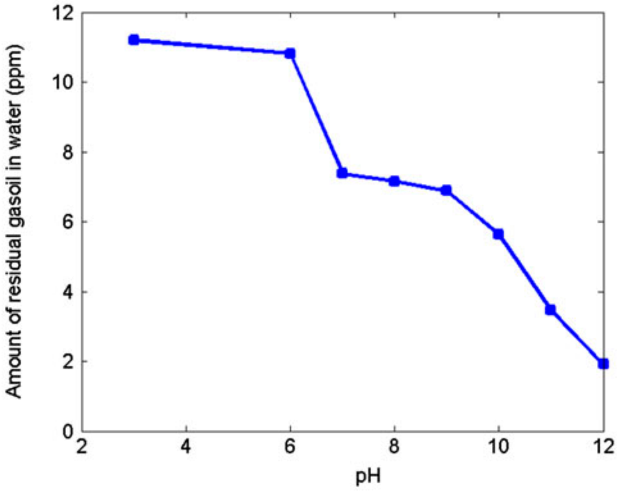

Fig. 8. Effects of pH on the adsorption of gasoil (1 g of SAC, $T = 25\,^{\circ}\mathrm{C}$, initial gasoil content = 1,000 mg/L in 50 mL water, 30 min mixing by rate 600 rpm).

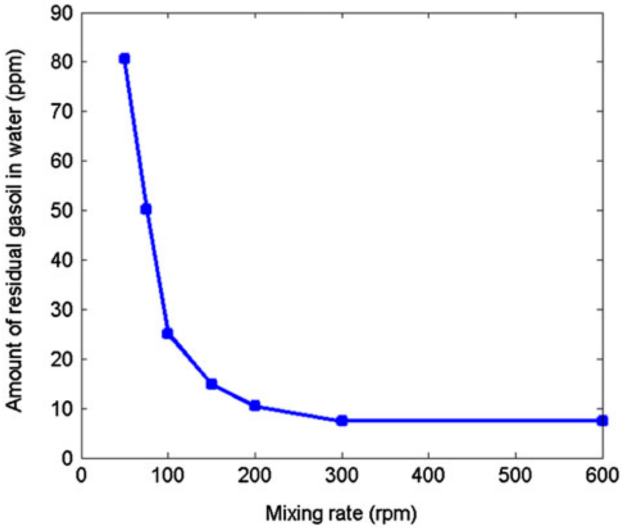

Fig. 9. Effects of mixing rate on the adsorption of gasoil (1 g of SAC, $T = 25\,^{\circ}\mathrm{C}$, pH = 7, initial gasoil content = 1,000 mg/L in 50 mL water, 30 min mixing).

2 ppm. pH affects the surface charge of adsorption and also by increasing the pH, the sticking of gas oil and SAC to the wall of the container and mixer reduces.

It is seen that in alkaline conditions the residual gasoil in water can be reduced to 2 ppm, a very low concentration and a fantastic recovery (near 99.8%), which may be required for special applications. However, like the effects of temperature, pH variations do not significantly change the adsorption performance of SAC and its recovery is always high in a wide range of pH.

### 3.6. Effects of mixing speed

The effects of mixing speed of polluted water and SAC were investigated by changing the mixing rate from 50 to 600 rpm. The other parameters were fixed the same as Section 3.3. Fig. 9 shows that the residual gasoil in water is reduced from 80 to 8 ppm by increasing the mixing rate from 50 to 600 rpm. Therefore, the mixing rate has a considerable effect on the adsorption performance. It is clear that higher mixing rates need more energy consumption; however, the time to reach equilibrium is lower instead.

### 3.7. Adsorption isotherms

Adsorption isotherms and equilibrium data describe how gasoil interact with SAC. The common isotherms that are most widely used are the Langmuir and Freundlich isotherms [21,22]. Langmuir isotherm assumes a homogeneous adsorbent surface whereby all active sites of adsorbent are identical. However, Freundlich isotherm is usually preferred to describe nonhomogeneous systems.

Langmuir model has successful application for monolayer adsorption process:

$$q_e = \frac{K_L C_e}{1 + bC_e} \tag{1}$$

where $q_e$ is the equilibrium gas oil concentration on the SAC (mg/g), $C_e$ is the equilibrium gasoil concentration in the water (mg/L), $b$ is Langmuir constant (L/mg), and $K_L$ is the Langmuir adsorption constant (L/g). Langmuir model can be rearranged to obtain an expression for a straight line as in the following equation:

$$\frac{1}{q_e} = \frac{1}{K_L} \times \frac{1}{C_e} + \frac{b}{K_L} \tag{2}$$

Fig. 10 shows the experimental data of $1/q_e$ versus $1/C_e$ for gasoil adsorption with SAC and the fitted line to find constants $K_L$ and b of Eq. (2). According to this figure it is seen that $1/K_L = 0.27$ (g/L) and $b/K_L = -0.021$.

Freundlich model is given by the following empirical equation:

$$q_e = K_F \times C_e^{\frac{1}{n}} \tag{3}$$

where $q_e$ and $C_e$ are the same as Langmuir model (Eq. 1), $K_F$ is the empirical Freundlich constant (mg/g), and $1/n$ is Freundlich exponent. Fig. 11 shows the

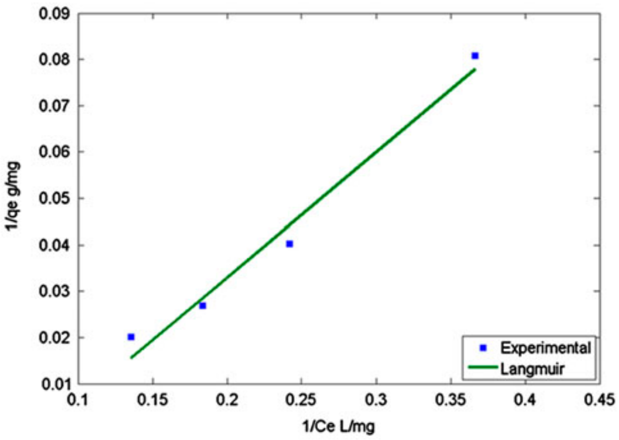

Fig. 10. Langmuir isotherms for gasoil onto 1 g SAC ($T = 25\,^\circ$C, pH = 7, 30 min mixing by rate 600 rpm).

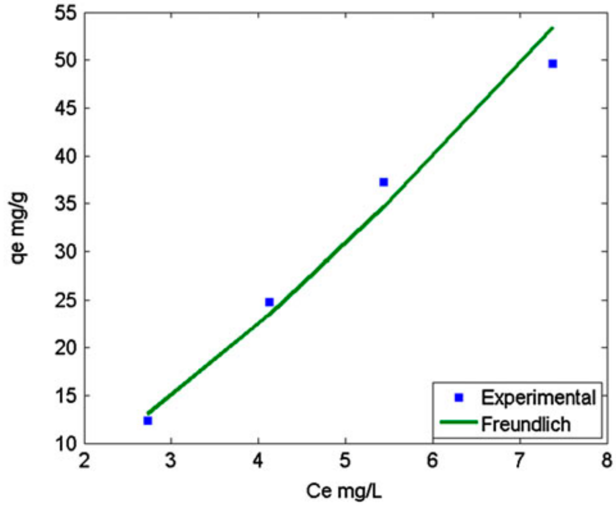

Fig. 11. Freundlich isotherms for gasoil onto 1 g SAC ($T = 25\,^\circ$C, pH = 7, 30 min mixing by rate 600 rpm).

fitted curve of Freundlich model using experimental data. According to this figure, $K_F = 3.1481$ (mg/g) and $1/n = 1.4161$.

Fig. 12 compares the results of the Langmuir and Freundlich isotherms with the experimental data. This figure reveals that the Freundlich isotherm can predict the adsorption of gasoil by SAC more accurately, especially at higher concentrations. This also concludes that the adsorption of gasoil onto SAC could be based on a nonhomogeneous and multilayer mechanism.

### 3.8. Regeneration of saturated SAC

Regeneration of clay is important for keeping the process cost down and also to recover gas oil that might be converted to useful products after processing.

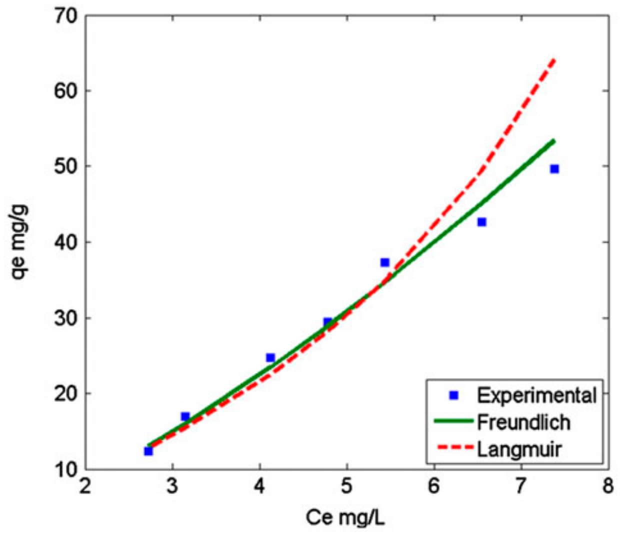

Fig. 12. Comparison of experimental results of gasoil adsorption onto SAC with different adsorption isotherms.

To have a saturated clay, 5 g of SAC was contacted with gas oil for 30 min. Then, the saturation of SAC with gas oil was measured, and it was found that the saturation is about 0.3608 g gasoil/g clay. Regeneration of saturated samples was investigated at four different temperatures (70, 90, 150, and 180 °C) and the results have been shown in the Fig. 13. The figure reveals that the regeneration of saturated SAC is incomplete at temperatures 70 and 90 °C. Regeneration performance improves by increasing the temperature to 150 °C; however, this temperature is still not enough for an acceptable degree of regeneration. However, Fig. 13 shows that SAC was almost completely regenerated by

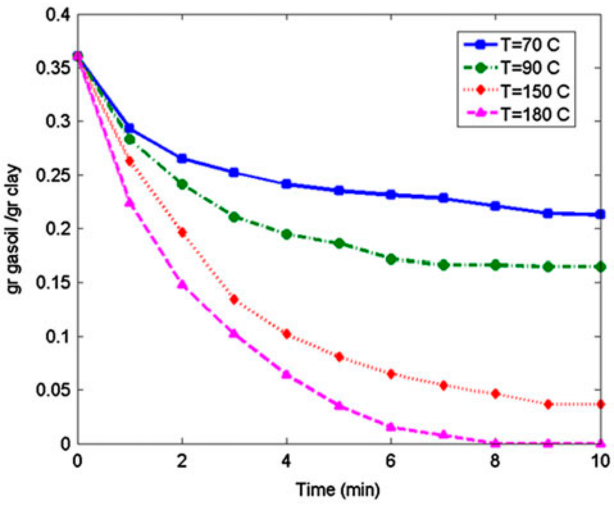

Fig. 13. Regeneration of Saturated SAC with gasoil at different temperatures.

Table 1
Gasoil adsorption by 1 g of regenerated SAC with different temperatures ($T = 25\,^\circ$C, pH = 7, 30 min mixing by rate 600 rpm)

| Temperatures of regenerated SAC (°C) | Initial gasoil in 50 mL water (ppm) | Final gasoil in 50 mL water (ppm) |
|---|---|---|
| 70 | 1,000 | 876.22 |
| 90 | 1,000 | 726.81 |
| 150 | 1,000 | 246.75 |
| 180 | 1,000 | 7.56 |

heating at a temperature of 180 °C after less than 10 min.

Regenerated samples at different temperatures were applied to check their adsorption performance. For each test, 1 g of regenerated sample was used to adsorb 1,000 ppm of gas oil in 50 mL of water and the other conditions mentioned in Section 3.3. Table 1 shows the results, and it can be seen that the regenerated SAC at 180 °C has a very acceptable adsorption, nearly the same as a fresh SAC. The other samples, regenerated at lower temperatures, do not have good adsorption recovery, which is due to their incomplete regeneration.

## 4. Conclusions

Three types of NCs and two commercial organoclays have been used to adsorb gas oil from wastewater. The initial results showed that one of them, called SAC, had a considerable recovery for gas oil removal from water. XRD analysis showed that SAC mainly contains PbO, which is one reason for the very good adsorption performance of this clay. Effects of temperature, pH, mixing time, rate of mixing, and dosage of SAC on the adsorption recovery of SAC were analyzed. Although all of these parameters affected the adsorption recovery, it was found that mixing time and rate of mixing were much more important factors. Langmuir and Freundlich isotherms were applied for the system and it was found that the Freundlich isotherm can predict the adsorption of gasoil onto SAC more accurately, especially at higher concentrations. Regeneration of saturated SAC was also studied and it was shown that this clay was almost completely regenerated by heating at 180 °C. Generally, this research shows that SAC is a powerful natural adsorbent with very high recovery and good regeneration. Therefore, based on its considerable specifications as well as its availability, this clay could be proposed for gasoil removal from wastewater in industrial applications.

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