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Insights into the remediation characterization of modified bentonite in minimizing organosulphur compounds from diesel fuel

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ABSTRACT

In this work, physical and chemical characteristics of the raw, treated, and acid activated bentonite were investigated using XRD, FTIR, scanning electron microscopy (SEM), and differential thermal analysis (DTA)/thermogravimetry (TG) analysis and surface area and porosity determination techniques. The organosulphur compounds (ORS) uptake was slightly affected by the particle size indicating that the removal of ORS mainly occurred on the external surface of the modified bentonite samples. The acid activation process enhanced the adsorptive efficiency of the bentonite sample through increasing both the surface area and the pore volume, in addition to the release of a considerable amount of interlayer cations of the clay.

Introduction

Many efforts are paid to minimize the environmental impacts stemming from the intensive use of petroleum fuels in different aspects of our daily life [1–3]. The intensive use of diesel fuel which occupies an important place among these fuels [2,4] poses some considerable technical and environmental problems due to its significant content of sulphur and nitrogen compounds. Some organosulphur compounds (ORS), for example, are known to be not only carcinogenic and mutagenic in animals and humans, but also cause catalyst poisoning and corrosion of equipment and engines. In addition, they are converted to sulphur oxides during combustion and form acid rains upon their contact with atmospheric water [2,5–11]. Typical ORS in diesel fuel portion, the boiling points varying in the range of 130–380 °C, are the alkylated benzothiophenes, dibenzothiophenes, and alkylated dibenzothiophenes [5,8]. Production of such fuels with low sulphur concentrations has been of main interest in petroleum industry [8,12]. Hydrodesulphurisation (HDS) processes, commonly used in refineries to reduce sulphur content in petroleum fuels, are based on the conversion of ORS to hydrogen sulphide (H_2S) and sulphur-free organic compounds upon reacting with hydrogen in the presence of catalyst(s), such as Co–Mo/Al_2O_3 and/or Ni–Mo/Al_2O_3. Although HDS has dominated desulphurisation of liquid fuels, it does not only require high temperature and pressure, use of expensive catalysts, and the economically undesirable large amounts of hydrogen consumption, but also reduced the lubricity arising from the saturation of the alkenes and arenes [7,13]. Because the fact that HDS is economically expensive, and it is not very efficient towards some benzothiophenes and dibenzothiophenes and some of their homologues [5], several research groups have been trying to develop alternative or complementary methods such as bioprocessing, oxidation, and direct adsorption for desulphurisation of diesel fuel and other liquid fuels [7,8,12–16].

In adsorptive desulphurisation, the petroleum based fuel is brought in contact with solid material that is able to retain considerable amount of sulphur-containing compounds as their polarity is higher than that of paraffinic, olefinic, and aromatic hydrocarbons. Since adsorptive desulphurisation can be applied at low temperature without external hydrogen supply, it could be seen advantageous, and complementary to HDS, especially if a cheap and easily available adsorbent could be employed [10,17–20]. Hydrophobic magnetic composites formed by carbon filaments on bentonite surface has been obtained via chemical vapour deposition of ethanol was synthesized by Mambrini et al. The

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hydrophobic bentonite was used as adsorbent of sulphur and nitrogen compounds, important contaminants in fuels, showing adsorption capacity of 38.7 mg g^{-1} and 54.5 mg g^{-1} for nitrogen and sulphur compounds respectively, a very high adsorption capacity compared with other materials with carbon presented in the literature.

Naturally occurring clay minerals, such as bentonite, are suggested to be good candidates as adsorbents for adsorptive desulphurisation because of their structurally induced adsorptive characteristics and low cost [21–23]. Bentonites which belong to the mica-like clay minerals of smectite-like layered structure are composed of a central sheet with octahedrally coordinated Al^{3+} or Mg^{2+}. Sheets with tetrahedrally coordinated Si which can be replaced in part by Al^{3+} cations are connected to the lower and the upper side of the central sheet by sharing common vertices of the coordination polyhedra (oxygen atoms).

The surface area of bentonite can be considerably enhanced via acid activation procedure. Thus, the partly removal of the central sheet where OH^- ions occur in the coordination sphere of the octahedrally coordinated cations through acid activation process leads to the modification of the adsorptive properties of bentonite significantly. The objective of the present study is to investigate in detail the physicochemical characteristics of the raw bentonite (RW), treated bentonite (TB), and acid activated bentonite (AB) samples. Furthermore, the competence of these adsorbents to remove the ORS will be ascertained by batch, kinetic and column studies. Another aim of the study is to investigate the effects of key factors such as particle size, temperature and initial total sulphur concentration on the adsorption phenomenon.

Experimental

Materials

Commercial diesel fuel (density: 0.84 g/mL) has been obtained from a randomly selected private gas station in Amman, Jordan. Diesel samples of different sulphur concentrations were prepared by sequential dilution of the commercial diesel fuel with n-heptane (Karl Roth®; Spectroscopic grade, density: 0.70 g/mL). The raw bentonite (RB), used in this study, has been provided by the Jordanian Natural Resources Authority from Al-Azraq region, Jordan. Analytical grade hydrochloric acid (Karl Roth®; 37%) has been used as received for the activation of bentonite.

Preparation of bentonite samples

The raw bentonite (RB)

The RB was ground into fine powdered samples. The air-dried RB samples were used for DTA/TG analyses while the oven-dried (at 105 °C overnight) samples were stored without further treatment for other characterization purposes.

The treated bentonite (TB)

The raw bentonite sample has been treated to reduce the amount of the silicate impurities (such as quartz) in RB, and to desalinate it as well, according to the following procedure [24]: (i) the RB sample was washed several times by distilled water, (ii) the resulting suspension was centrifuged at 750 rpm for 3 min to separate quartz and other silicate components. The supernatant solution was carefully decanted off and collected into a large bottle afterwards. This procedure was repeated several times, and (iii) the bentonite was separated from excess water by settling down the suspension, and then dried at 105 °C for overnight, ground and sieved to the particle sizes of 710–500 μm, 500–300 μm, and 300–150 μm in order to use TB as adsorbent, while the fine powdered, air dried TB samples were stored for DTA/TG analyses.

The activated bentonite (AB)

Considering the nature of the bentonite in study, the following acid activation procedure was applied for activating the local bentonite to improve the surface properties such as specific surface area and adsorption capacity [21,25–27]. The bentonite sample of 100 g was first dispersed in a sufficient volume of deionised water, and then 600 mL of 3 M HCl (37%) was added to the suspension. The mixture was continuously stirred under reflux for 12 h at 70 °C and then cooled down to room temperature. The activated bentonite was separated by suction filtration, using Whatman® qualitative filter paper (grade 3), and washed several times with deionised water until no more chloride ions could be detected (Silver nitrate test). The activated bentonite thus obtained was dried at 105 °C in an oven for overnight and then ground to necessary particle size and kept for characterization and adsorption processes. For TGA/TG studies, the air dried samples were used instead.

Instrumentation

X-ray diffraction patterns of the RB, TB, and AB samples were recorded with the scanning speed of 0.4° 2θ s^{-1} using (HZG4-ID 300) powder diffractometer, operated at 40 kV and 37 mA, using Mn filter and an X-ray beam of wavelength of 1.9373 Å produced using Fe anode. The samples were dried and ground into fine powder prior to characterization. Diffraction patterns were interpreted by comparison with the standard patterns stored in the instrument library. The chemical compositions of the RB, TB and AB samples were determined by X-ray fluorescence (XRF)

Table 1
Chemical compositions of RB, TB, and AB.

Sample	RB	TB	AB
SiO_2 (%)	54.18	53.13	62.42
Al_2O_3 (%)	13.67	15.33	16.79
Fe_2O_3 (%)	9.97	13.31	12.34
Na_2O (%)	3.27	4.67	0.65
MgO (%)	6.61	5.71	3.16
CaO (%)	8.26	3.74	0.55
K_2O (%)	2.26	2.18	1.95
TiO_2 (%)	1.34	1.01	1.44
MnO (%)	0.03	0.03	0.02
P_2O_5 (%)	0.06	0.05	0.06
LOI (%)	13.55	12.11	7.37

Representative XRD peaks of the RB

Mineral (constituent)	2θ	d-Spacing
Montmorillonite	34.74	3.24
	31.50	3.57
	9.90	11.23
	35.30	3.19
	24.98	4.48
	24.66	4.54
	17.18	6.49
	22.54	4.96
	44.38	2.56
	79.86	1.51
Stevensite	38.98	2.90
	16.34	6.82
	52.22	2.20
Saponite	30.46	3.69
	37.3	3.03
	64.42	1.82
Quartz	33.66	3.35
	26.3	4.26
	50.22	2.28
Nontronite	40.22	2.82
	44.02	2.58
	46.50	2.45
	65.38	1.79
Iron oxide	57.30	2.02

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