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Evaluation of the potential of volatile organic compound (*di-methyl benzene*) removal using adsorption on natural minerals compared to commercial oxides

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HIGHLIGHTS

- The adsorption of dMB on natural minerals and commercial oxides was evaluated.
- The adsorption capacities were discussed considering the adsorbents cost and the bed size.
- The adsorption capacity of bentonite is higher than other adsorbents.
- Langmuir model provide best correlation of the experimental data.
- The isotherms data allow determination of isosteric heat of adsorption.

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ABSTRACT

This study is dedicated to the investigation of the potential of volatile organic compounds (VOC) adsorption over low cost natural minerals (bentonite and diatomite). The performances of these solids, in terms of adsorption/desorption properties, were compared to commercial adsorbents, such as silica, alumina and titanium dioxide. The solids were first characterized by different physico-chemical methods and di-methyl benzene (dMB) was selected as model VOC pollutant for the investigation of adsorptive characteristics. The experiments were carried out with a fixed bed reactor under dynamic conditions using Fourier Transform InfraRed spectrometer to measure the evolution of dMB concentrations in the gaseous stream at the outlet of the reactor. The measured breakthrough curves yields to adsorbed amounts at saturation that has been used to obtain adsorption isotherms. The latters were used for determination of the heat involved in the adsorption process and estimation of its values using the isosteric method. Furthermore, the performances of the studied materials were compared considering the adsorption efficiency/cost ratio

1. Introduction

Volatile organic compounds (VOCs) are among hazard chemicals pollutants emitted by industrial processes involving solvents, detergents, degreasers, cleaners and lubricants [1,2]. They are often toxic or carcinogenic and their elimination, at a reasonable cost, is a serious challenge not only for many industrial processes [3–5] but also as response to increased environmental awareness and stringent regulations of pollutants emission [6–9]. A numbers of techniques such as condensation, thermal oxidation, catalytic oxidation, biofiltration, absorption and adsorption have been developed for the removal of VOCs [10–12]. Among these techniques, adsorption process is considered as proven and reliable alternative technology, due to related lower required energy and cheaper operating costs [12–19].

Several adsorbents have been extensively studied for VOC abatement, such as silica gel [3,20], zeolites [8,21–26], mesoporous materials [27–33] and activated carbons [34–36]. Among them activated carbon is the most widely used in industrial applications regarding its higher adsorption capacity and lower cost [29]. However, activated carbons have the drawbacks associated with added fire risk, hygroscopic with pore clogging, and regeneration difficulties [37–41].

On the other hand, hydrophobic zeolites are on average ten times more expensive and sensitive to the presence of humidity.

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For these reasons, it is important to investigate VOC adsorption/desoprtion performances of other potential materials with highier capacity, good stability, low cost, and regeneration possibilities.

Natural clays might be considered for abatement of VOCs fom waste gases regarding their low cost, physicochemical properties and texture. Such characteristics make them of interest for the abatement of VOCs. So far, few reports have been published on VOCs adsorption on natural [42–46], and modified clays [47,48].

The materials investigated in the present study, namely diatomite and bentonite (denoted DT and BT) were compared to commercial Al_2O_3, SiO_2 and TiO_2 with aim of evaluation of their potential as adsorbent for the removal of organic VOC contaminants. Di-methyl benzene (denoted dMB) was selected as model VOC based on the following criteria: (a) it belongs to the U.S. Environmental Protection Agency EPA's priority pollutant list [49], and (b) it is generated by petrochemical industries [50], catalytic processes isomerization [51,52] and oxidation [53].

In the present work, the adsorptive properties were compared by taking into account the ratio efficiency/cost and the ability of the solids to be easily regenerated based on values of isosteric heat of dMB adsorption.

2. Experimental

2.1. Adorbents and adsorbate

The adsorbents, used for the adsorption of VOCs, were local raw a mineral (diatomite and Bentonite) from Nador province in Morocco. The solids Al_2O_3, SiO_2 and TiO_2 were supplied by Degussa Company. The solids were dried in air at 423 K for 24 h before use as adsobent. The same sample was used for several sets of experiments and were pretreated before each adsorption as follows: (a) for raw mineral: N_2, 300 K → N_2, 423 K (1 h) → N_2, 300 K and (b) for commercial materials: N_2, 300 K → N_2, 673 K (1 h) → air, 673 K (1 h) → N_2, 673 K (10 min) → N_2, 300 K.

The di-methyl benzene (purity >99%) was from Sigma–Aldrich and N_2 was supplied by Air Liquid.

2.2. Textural characterisations

The surface areas and pore volumes of the adsorbents were measured by an automatic volumetric sorption analyzer (Micromeritics model Asap 2000) using N_2 adsorption at 77 K.

The morphological analysis was carried out with Scanning Electron Microscopy (SEM) (Hitachi S800 FEG). The chemical composition of the two minerals was determined using a fluorescence spectrometer (Brucker S4 Piooner). The thermal stability of the solids was studied with A.T.G, D.T.G experiments using Setaram 92 apparatus.

2.3. Design of the adsorption/desorption (Ads/Des) experiments

The adsorption/desorption experiments were carried under dynamic conditions at atmospheric pressure with a homemade setup, as previously reported [43]. Briefly, 0.1–1 g of adsorbent were introduced in a quartz microreactor as small meshes with diameters between 200 and 400 μm, using a total flow rate of *x*% dMB/N_2 of 100 mL/min (residence time <0.1 s) using a mass flow controller (Brooks).

The experimental data of the adsorption of dMB were obtained as follows: after the pretreatment in a gas flow rate of N_2, the solid was cooled down to 300 K and a gas flow rate (100 mL/min) of a *x*% dMB/N_2 gas mixture with ($x < 1$) fixed by a conventional Pyrex saturator/condenser system was introduced according to a switch N_2 → *x*% dMB/N_2. The molar fractions of the dMB (after calibration using dMB/N_2 gaz mixtures of know compositions) at the outlet of the reactor were followed with time on stream using a home made Pyrex gas IR cell with CaF_2 windows equipped on a Jasco FTIR spectrometer. After the adsoption equilibrium, the isothermal desorption was studied using the switch: *x*% dMB/N_2 → N_2, whereas the evolution of the molar fraction of dMB was continuously monitored with the FTIR spectrometer. After obtaining a very low concentration of dMB in the flow (very low rate of isothermal desorption), the sample was heated according to Temperature Programmed Desorption (5 K/min) method in order to desorb the remaining amount the adsorbed dMB.

3. Results and discussion

3.1. Textural and chemical characterization of the different solids

3.1.1. BET surface area and porosity

The N_2 isotherms obtained with different natural solids shown in Fig. 1 were mainly of type IV according to the IUPAC classification [54]. In a high relative pressure range, the isotherms show a clear hysteresis loop associated with capillary condensation taking place in mesopores structures, formed between the elementary clay particles named tactoids [55–57].

As shown in Table 1, BET surface areas of the natural and commercial samples were 83.5, 21, 107, 55 and 200 m^2/g for BT, DT, Al_2O_3, TiO_2 and SiO_2 respectively. All samples exhibits an overall mesoporous structure with an average pore diameter ranging from 6 to 11 nm.

Table 1 provides the most relevant textural properties of the adsorbent materials used in the present study.

3.1.2. Chemical composition of solids

The chemical composition of the samples was determined with Brucker S4 Piooner spectrometer. Table 2 shows that for bentonite and diatomite are mainly constituted of silica, alumina, and calcium

Table 1
Textural parameters of five adsorbents.

Solids	S_{BET} (m^2/g)	V_t (cm^3/g)[a]	V_{meso} (cm^3/g)[b]	S_{ext} ($m^2/g\,g$)[c]	$S_{mic\,equi}$ (m^2/g)[d]	V_{mic} (cm^3/g)[e]	D_p (nm)[f]	d_p (g/cm^3)
BT	83.5	0.213	0.212	81.024	2.4691	0.0005	10.2	0.55
DT	21	0.035	0.0326	15	6	0.0024	6.8	0.326
Al_2O_3	107	0.2	0.19	94.64	12.86	0.011	7.47	0.05
SiO_2	200	0.43	0.4298	198.53	1.47	0.0002	4.4	0.05
TiO_2	55	0.1628	0.1606	49.62	5.6	0.0022	8.5	3.5

[a] Total pore volume.
[b] Mesoporous volume.
[c] External specific surface.
[d] Specific micropore surface area.
[e] Microporous volume.
[f] Pore diameter, d_p: apparent density.