



Adsorption of hydrocarbons from industrial wastewater onto a silica mesoporous material: Structural and thermal study



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ABSTRACT

In this paper, the use of a mesoporous silica alumina (MSA) for the removal of hydrocarbons from water is outlined. In particular, we focused our attention on the structural modifications that occur during the adsorption process using toluene and benzene as target contaminants and two different material shapes: particle and extruded. Different characterization techniques such as SEM, powder XRD, TGA and IR absorption are used to gain a deep investigation of MSA characteristics. Indeed, morphological features of MSA, the thermal behavior of the loaded and unloaded material including its regeneration and host–guest interactions were largely examined. SEM images and EDX analysis of the two materials have confirmed their amorphous nature and their elemental composition. Powder XRD patterns of as-synthesized (unloaded) and loaded MSA displayed the appearance of some reflection peaks after the adsorption of benzene and toluene. A Le Bail refinement indicated a monoclinic structure for these molecules when adsorbed onto the MSA. FT-IR measurement on loaded and unloaded MSA highlighted the interaction of water with the free silanol groups while the aromatic hydrocarbons probably adsorbed onto different active sites (Lewis acid sites). Indeed, intrinsic acidity measurements by pyridine adsorption showed the presence of a fairly good number of these acid sites. Finally, the thermal behavior of loaded MSA samples with different contaminants has shown the strong influence of water on the desorption temperature of pollutants from MSA.

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1. Introduction

Recovery of waste water is one of the most important challenges for our future due to the endemic scarcity of this resource in many parts of the world. Waste waters derived from petrochemical activities represent a large share of water linked to human activities. During the oil extraction phase, a large amount of waste water is produced [1]. It is naturally present in the deposit rock and extracted with the oil, forming an emulsion. After the separation operation, the oil is sent to the refining units where water is stocked, usually in exhausted wells or pumped in the same well of its extraction to keep the high pressure required for oil extraction. This wastewater is very rich in insoluble and soluble hydrocarbons such as short chain ketones, aldehydes and/or phenols. It is also characterized by high salinity and by the presence of heavy metal ions such as Pb^{2+} , Cd^{2+} , Ni^{2+} , $Cr_2O_7^{2-}$ and VO_3^+ , typical of the

geochemistry of the deposit rock and of the chemical composition of the ancestral organic matter [2–4]. Several primary treatments, including oil separation, coagulation, flocculation, flotation and filtration have been successfully used to remove oil and suspended solids from produced water [5–7]. Biological treatments, also known as secondary treatments, should also be considered when these effluents are discharged into natural receiving bodies [8,9]. For instance, approximately 145 million cubic meters of water were utilized in 2005 in the Canadian state of Alberta for the extraction of oil from oil shale [10], and in the USA refining operations use approximately 16 million liters of water per year [11]. Concerning this data, it is needful to reuse this waste water at least for the same activities. In addition to the extraction water, another large amount of water is used during the refining activities. This water might be rich in hydrocarbons if it is used in a steam reforming unit or distillation tower, or rich in inorganic and heavy metal ions if it is used in a desalting unit.

The presence of the refineries is linked to the contamination of the groundwater by heavy and light hydrocarbons and sometimes

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heavy metals. In addition to this, the oil refineries are in many cases located along the coasts, and high salinity of seawater may represent a further problem in the remediation of the contaminated groundwater. Currently the large use of hydrofracking technology is spreading, especially in the USA [12]. This kind of technology is based on the fracturing of the deposit rock to release and collect gas and oil; this is easier than by the traditional methods. Fracking cannot be classified as a “green” process and usually causes the contamination of the groundwater adjacent to the deposit rocks [13]. The use of adsorption technologies to recover waste water for all the petrochemical activities is a very useful technology, especially by using active carbon as the adsorbent material [14,15]. Active carbon is the traditional adsorbent used for water remediation and can be produced from several vegetable sources, such as coconut shells or cellulosic waste, or more traditional sources, such as carbon and wood [16,17]. However, its usage has important disadvantages in terms of selectivity and regeneration. The first is a consequence of the aqueous medium in which active carbon has to operate. Water molecules are strong competitors for the active sites of the active carbon, such as the alcoholic and carboxylic ones, and water has the particular ability to drench the carbon pore, preventing the adsorption of contaminants. Regarding selectivity, major problems might be encountered in the remediation of groundwater which can be relatively rich with humic substances. These substances are formidable interfering agents because they are able to interact strongly with the adsorption sites of the activated carbon [18]. Regeneration problems may take place, especially in cases where very high regeneration temperatures are used. In these cases, the high temperature might promote sintering of the material, condensation of the active sites, collapse of the internal structure and consequently a decreasing of the subsurface area with loss of material by burning [19]. Furthermore, if carbon is used with high salinity water, this kind of regeneration does not guarantee the elimination of the adsorbed inorganic ions. To overcome these disadvantages, in the last decades different materials have been developed such as synthetic zeolite, mesoporous materials and the newest MOFs. In particular, the zeolite materials are more stable at high temperature and more selective; moreover, they can be modified with specific ligands to increase selectivity and stability [20]. A process for treatment of wastewater contaminated by organic compounds by adsorption on hydrophobic (siliceous) zeolites has been recently reported [21]. Quite good results have been described in case of dissolved hydrocarbons, while reduced effectiveness has been noticed in presence of oil droplets due to pore clogging. In particular, the mesoporous materials seem to be very effective for hydrocarbon removal both in emulsion and in solution [22]. Their large pore size is more suitable to host large organic molecules, allowing the functionalization of the material with a wide variety of hindered ligands and improving their chemical and physical stability as well as adsorption performances [23]. In a previous study [22] was evaluated the adsorption of toluene and benzene onto a new mesoporous material, the MSA (mesoporous silica-alumina), in order to recover wastewater derived from extraction and oil refining. In that study, it was shown that toluene is more adsorbed than benzene, probably due to the presence of the methyl group on the aromatic ring of toluene. The methyl group might hinder toluene to freely rotate in each direction during the adsorption while benzene, devoid of substituent, is more mobile and less adsorbed. In this paper, attention was focused on understanding which kind of interaction takes place between the contaminants and the material (studied in two different shapes, extruded and particle) as well as the role of water during the adsorption process. The thermal behavior of the MSA was also successively examined in order to test the strength of the adsorbent–adsorbate interactions and know the desorption temperatures of the adsorbed contaminants.

2. Experimental section

2.1. Materials

The mesoporous material was developed and synthesized by eni S.p.A. [24,25]. MSA adsorbents were synthesised via sol–gel in alkali-free medium using $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Dynasil-A, Nobel), $\text{Al}(\text{sec-OC}_4\text{H}_9)_3$ (Sigma–Aldrich®), tetrapropylammonium hydroxide (TPA-OH, Sachem), alcohol (R-OH) selected among $\text{C}_2\text{H}_5\text{OH}$ or $n\text{-C}_3\text{H}_7\text{OH}$ (Aldrich). All preparations were performed at the same molar ratios: $\text{TPA-OH}/\text{SiO}_2 = 0.09$, $\text{H}_2\text{O}/\text{SiO}_2 = 8$ and $\text{alcohol}/\text{SiO}_2 = 8$. A typical synthesis preparation is described: $\text{Al}(\text{sec-OC}_4\text{H}_9)_3$ was dissolved in $\text{Si}(\text{OC}_2\text{H}_5)_4$ at 60°C . The obtained homogeneous solution was cooled at room temperature, and then the required alcohol and TPA-OH in aqueous solution were added in sequence. Monophasic clear solutions were obtained, and then transformed in homogeneous compact gel without separation of phases. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ (SAR) molar ratio and the selected alcohol are reported in Table 1 for each preparation. After 15 h ageing at room temperature, the gels were dried at 100°C and calcined 8 h in air at 550°C . MSA samples textural characterisation was carried out by nitrogen adsorption at -196°C on Micromeritics ASAP 2010 apparatus. Before determination of adsorption–desorption isotherms the samples (~ 0.2 g) were outgassed for 16 h at 350°C under vacuum. The MSA synthesized and studied in this work was amorphous with a low degree of long-range order in terms of pore disposition. The extruded MSA was obtained by a post-synthetic modification of particle MSA, extruding the MSA particles into cylindrical shape, using Al_2O_3 as binder. In Table 1, the main physical characteristics of the particle and extruded MSA are shown. Apparent specific surface area (A-SSA, Brunauer Emmett and Teller method), specific pore volume (V_p , Gurvitch rule) and mean pore size (D_p , non-local density functional theory algorithm) were evaluated from the acquired isotherms. Before water treatment experiments, materials were sifted between 0.12 and 0.5 mm and calcined at 550°C for 8 h.

2.2. Adsorption tests

The adsorption tests were carried on both materials using toluene and benzene as target contaminants. Aqueous solutions of these hydrocarbons were prepared at a concentration as high as possible paying attention to not overcome their solubility limit; in this way, we chose to operate at 400 mg/L of toluene and 800 mg/L of benzene. Each solution (50 ml) was kept in contact with 0.05 g of MSA with rotative stirring for 24 h to ensure the attainment of the equilibrium state. Tests using an emulsion of diesel oil in water were performed in order to have information about the behavior of the MSA in a situation closer to reality. Afterwards, each sample was filtered and the solid material was analyzed by X-ray diffractometry (XRD), Fourier transformed Infra-Red spectrometer (FT-IR), Thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). To investigate the nature of the host–guest interaction and the role of the water in the adsorption phenomenon, the same type of analyses were performed on the material before the adsorption tests. Finally, analyses on pure adsorbed contaminants (benzene and toluene) have been made to distinguish which kind of interactions are due to organics, water and water-organic mixture.

Table 1
Textural properties of particle and extruded MSA.

Adsorbent	SAR	A-SSA (m^2/g)	Alcohol	V_p (ml/g)	D_p (Å)
Extruded MSA	∞	487	$\text{C}_3\text{H}_7\text{OH}$	1.06	51
Particle MSA	∞	233	$\text{C}_3\text{H}_7\text{OH}$	0.52	98

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