



Microporous and mesoporous materials for the treatment of wastewater produced by petrochemical activities



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ABSTRACT

The recovery of wastewater will be a fundamental action in the coming years to facilitate the sustainable development of the world's economies. A large portion of recoverable wastewater comes from petrochemical activities such as oil extraction and its subsequent refining processes. The most important characteristic of this water is its heavy contamination by soluble and insoluble hydrocarbons (as emulsified hydrocarbons) and inorganic and heavy metal ions. Furthermore, the presence of refineries is directly linked to possible groundwater contamination that must be then remediated. In this context, adsorption technologies appear to be very promising for the remediation and recovery of "petrochemical" water. In this paper, we present a review of applied adsorption technologies and examine both the use of two different microporous materials, a natural zeolite called clinoptilolite and a polymeric chelating resin named Purolite[®] Resin S910, for the removal of dissolved heavy metals, and the use of a mesoporous siliceous material for the uptake of hydrocarbons from wastewater. Batch experiments on the kinetics and equilibrium of adsorption were carried out on all the materials by using Pb²⁺, Cd²⁺ and Ni²⁺ as target heavy metals and benzene and toluene as target organic pollutants. The effect of ionic strength was also investigated.

The batch tests indicated a good adsorption rate and a percentage of heavy metal and hydrocarbon removal that was always greater than 90%. A new adsorption model was also developed to better describe the adsorption mechanism of heavy metals, while a model with a two-step mechanism was chosen for hydrocarbons. Increasing ionic strength appeared to decrease the adsorption performance of the microporous material and the presence of organic interfering contaminants. However, both materials seemed to maintain good adsorption capabilities.

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1. Introduction

The world is facing a water crisis due to rapid industrial development and the resulting major quantity of noxious compounds discharged into water systems. It has been estimated that nearly 80% of the world's population is exposed to high levels of threat to its water security (Voeroesmarly et al., 2010).

Within this framework, polluted water remediation should be considered a major challenge (Khan et al., 2004).

The energy industry is one of the main actors in this scenario: produced water is by far the largest waste stream by volume associated with oil and gas exploration and production (Ahmadun

et al., 2009). Such water is trapped in underground formations and brought to the surface along with oil or gas. The volumetric ratio of produced water to oil depends on the reservoir geology, age and exploitation technology used, but values ranging from 2 to 3 (with peaks of 50) have been reported worldwide. The main produced water pollutants are oil and grease, chemical additives, natural compounds (both organic and inorganic) and naturally occurring radioactive materials.

Groundwater pollution is a further emergency related to ineffective waste management, widespread dispersion of chemicals (e.g., due to chemical-intensive industries, fuel production and storage and crop protection operations) or the natural release of noxious compounds from rocks and soils.

Groundwater can be pumped to surface treatment facilities (such as those based on columns packed with active materials) using a pump and treat (P&T) approach. The use of permeable

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reactive barriers (PRBs) has been suggested as an alternative (Richardson and Nicklow, 2002). In this case, walls of active material are sunk directly into the plume, forming active cells. These structures are then covered with clean soil, allowing safe property exploitation while remediation is still in progress. Depending on the specific case, pollutants may be trapped in situ by sorption or converted into non-hazardous compounds by chemical or biological routes (Scherer et al., 2000).

Adsorbents based on zeolites, silica-aluminas and silicas have drawn interest from both industry and academia due to their verified and potential effectiveness in water remediation (Perego et al., 2013).

In particular, zeolites have been proposed to take advantage of their peculiar characteristics, which include i) high selectivity due to a strictly defined chemical composition and porous texture; ii) tunable hydrophilicity; iii) proven stability under harsh conditions; and iv) in most cases, excellent regenerability (Weitkamp, 2000). Zeolites are microporous crystalline solids (i.e., with pore diameters not exceeding 2 nm (Sing et al., 1985)), and the zeolite framework is based on a three-dimensional network of corner-sharing [TO₄] tetrahedra, with T usually corresponding to silicon and aluminum. The material is characterized by the presence of regular voids capable of allowing the adsorption and diffusion of ions and molecules. Zeolites found in nature and their synthesized counterparts can be broadly categorized according to their silicon vs. aluminum molar ratio (SAR), with those having SAR values higher than 5 mol/mol being more hydrophobic (i.e., less hydrophilic) compared to those with lower SAR values (Breck, 1974). The presence of aluminum in the framework induces negative charges compensated by loosely bound cations that can be exchanged with each other. Zeolite minerals (e.g., clinoptilolite, chabazite, or mordenite) are available in large quantities in natural deposits, so they are commonly considered low cost adsorbents that are quoted at less than 1 USD/kg. These minerals are generally aluminum-rich, making them hydrophilic. Indeed, cation-exchange is one of the oldest applications of these adsorbents in the field of environmental protection, with particular reference to heavy-metal-cation removal (Wang and Peng, 2010). The study of cation-exchange thermodynamics has pointed to both zeolite characteristics and cation water chemistry as factors influencing its adsorbent selectivity (Caputo and Pepe, 2007). Major quantities of natural zeolites were employed to adsorb dangerous radio-nuclides (mainly ¹³⁷Cs and ⁹⁰Sr) after the Chernobyl (Ukraine) and Three Mile Island (USA) disasters, and their implementation in the field of nuclear waste management continues to draw interest today (Misaelides, 2011). Natural and synthetic zeolite performances have been described in (Seliman and Borai, 2011) and (Borai et al., 2009), respectively, and the effectiveness of the former has been noted despite its low cost. The use of zeolite monoliths for radio-nuclide removal from marine water has also been evaluated recently through lab-scale trials simulating water leaks from the damaged Fukushima (Japan) reactor (Sachse et al., 2012).

Ammonium rejection by cation-exchange on natural zeolites has been considered an option for implementation in conditions adverse to biological treatment (e.g., the co-presence of biological inhibitors, nutrient scarcity, or low temperature) (Hedstroem, 2001). From a mechanistic perspective, it has been demonstrated that cation-exchange occurs through sites located inside zeolite pores (Garcia Basabe et al., 2012).

In practice, several factors have been identified as influencing cation-exchange performance: i) zeolite framework structure; ii) zeolite framework electrostatic field strength; iii) cation charge density; iv) contact solution composition; v) contact solution pH; vi) raw mineral composition and work-up; and vii) process apparatus and operating conditions (e.g., continuous stirred tank

vs. fixed bed column). With so many factors, the reported comparison of results can be extremely difficult and often contradictory.

Synthetic zeolite-like adsorbents based on corner-sharing [SiO₄] tetrahedra, [TiO₅] pentahedra or [TiO₆] octahedra (e.g., ETS-4, ETS-10, ETAS-10, bearing negative charges on titanium) have been successfully employed in lab-scale experiments as heavy metal cation-exchangers. Evidence of the effective adsorption of Cd²⁺ (Otero et al., 2009), Pb²⁺ (Choi et al., 2006; Zhao et al., 2003) and Hg²⁺ (Lopes et al., 2011) have been reported. Unfortunately, titanosilicate's poor stability under acidic conditions has been stressed as a relevant issue (Krisnandi et al., 2006).

Several exhausted zeolitic cation-exchanger regeneration approaches have been described, including sweeping with aqueous solutions containing mineral acids, inorganic salts or complexing agents.

Zeolite's affinity towards anions and non-dissociated compounds is far lower, requiring adsorbent modifications or, at the least, careful selection.

Lab-scale experiments regarding anion-exchange have been described on zeolites modified with metal ions. Specifically, modifiers such as Al³⁺, La³⁺, ZrO²⁺ (Samantya et al., 2007), Na⁺, Ca²⁺, and Eu³⁺ (Diaz Nava et al., 2002) have been studied for fluoride removal, while Al³⁺ (Xu et al., 2002) and Fe³⁺ (Davila Jimenez et al., 2008) have been studied for arsenic oxo-anions. Exchange among anions in solution and hydroxyls on an adsorbent surface (Xu et al., 2002) or anion inclusion into pores (Liu et al., 2011; Villacusa et al., 2002) have been inferred as possible mechanisms. On the other hand, oxides of aluminum (Choi and Chen, 1979), iron (Aredes et al., 2012) and magnesium (Sasaki et al., 2013) have also been used for anion adsorption. Sweeping with aqueous solutions containing mineral bases has been described as a possible regeneration approach.

Encouraging results concerning both anion (e.g., nitrogen, chromium, selenium oxo-anions) and non-dissociated compound (e.g., hydrocarbons and their derivatives) removal have been reported for adsorbents based on clinoptilolite zeolite modified with surfactants based on organic ammonium salts. Such surface-modified zeolites (SMZs) have been successfully implemented through the pilot scale according both to the PRB (Bowman, 2003) and P&T (Ranck et al., 2005) approaches.

Interestingly, surface modification has had a minimal influence on cation-exchange features due to the bulky surfactant molecules' inability to diffuse into zeolite micro-pores where most of the active sites are located (Baeza Alvarado and Olguin, 2011). Following these results, SMZs have been considered multi-purpose adsorbents capable of targeting the following: i) cations at zeolite framework exchange sites; ii) anions, through interaction with surfactant molecule hydrophilic heads; and iii) non-dissociated compounds, through partitioning into surfactant molecule hydrophobic tail bundles.

Effective regeneration by air sparging has been experienced with SMZs exhausted with volatile organic non-dissociated compounds, and to our knowledge, a regenerability approach for SMZs exhausted with inorganic salts has not been defined. Relevant surfactant leaching has also been witnessed (Altare et al., 2007). Such release has been identified as a potential source of economic losses and environmental pollution (Schick et al., 2011).

Siliceous synthetic zeolites have been suggested to combat this drawback. In particular, the effectiveness of silicalite, mordenite (Anderson, 2000) and beta zeolites (Abu Lail et al., 2010) as adsorbents for non-dissociated compounds has been tested in both lab-scale and full-scale (Vignola et al., 2011a) tests. The sorption performances (in terms of both specific capacity and stability under realistic operating conditions) have been verified as better than

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