



Ionic-liquid-crafted zeolite for the removal of anionic dye methyl orange



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ABSTRACT

In this study a clinoptilolite zeolite was modified by an ionic liquid 1-hexadecyl-3-methylimidazolium chloride monohydrate to 1.0 and 2.0 times its external cation exchange capacity (ECEC). The ionic-liquid-crafted zeolite (ILCZ) was tested for its removal of anionic dyes from solution using methyl orange (MO) as an example. The uptake of MO was fast and followed a pseudo-second-order kinetics with MO adsorption capacities of 45 and 116 mmol/kg on ILCZ modified to 1.0 and 2.0 ECEC, respectively. Stoichiometric desorption of counterion chloride accompanying MO uptake suggested an anion exchange mechanism of MO uptake on ILCZ modified to 2.0 ECEC. Solution pH in the range of 2–11 and ionic strength in the range of 0.001–0.01 M of background salt concentrations of varying charges had minimal effects on MO uptake, suggesting higher affinity of MO for ILCZ in comparison to other inorganic anions. As the MO adsorption capacity on ILCZ modified to 2.0 ECEC was about the same as the ECEC of the zeolite, the mechanism of removal of anionic dyes was attributed to surface anion exchange resulted from the positively charged ILCZ surfaces due to a bilayer IL formation on zeolite after being modified to 2.0 ECEC. In contrast, patchy admicelles of IL would form on zeolite after being modified to 1.0 ECEC, resulting in reduced MO uptake. The contrasting behaviors of IL modification on zeolite and subsequent MO adsorption on ILCZ suggested that modification of ILCZ to 2.0 ECEC was necessary for ILCZ to serve as a sorbent material for the removal of anionic dyes from solution.

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1. Introduction

Dyes are an important class of synthetic organic compounds used in many industries, especially those used in textiles [1]. The textile industry consumes huge amounts of water, creates remarkable amounts of wastewater, and the dye effluents are responsible for major environment concerns in wastewater treatments [2]. Methyl orange (MO) is an anionic dye. Because of its stable structure, it is not easily degraded [3,4]. Thus, many techniques were developed for the removal of MO from wastewater. The common ones include ion exchange, H₂O₂ and Fenton reagents, photocatalytic degradation, and chemisorption [5], with chemisorption as the most effective method [6]. Activated carbon (AC) derived from different types of raw materials was also tested for the removal of MO [7,8].

Commonly used sorbent materials should be of high stability and adsorption capacity, and be inexpensive in material cost. Thus, earth

materials were studied extensively as the sorbents for contaminant removal from water. Montmorillonite (MMT) and zeolite, due to their wide distribution and availability, large surface area, high cation exchange capacity (CEC), and inexpensive material cost, have been applied for the removal of contaminants of different types. Although raw MMT had limited affinity for acid dyes, acid activation could increase its MO sorption capacity by a factor of 8 [9]. A raw bentonite whose major mineral composition is MMT had an MO sorption capacity of 34 mg/g at pH 4 and the unusually large value was attributed to hydrogen bonding [10]. A similar MO sorption was found on another bentonite and was attributed to strong hydrophobic interaction [11]. The presence of humic acid could decrease MO sorption while the presence of MO was able to enhance humic acid sorption on bentonite [11].

Due to a general lack of positive charges for earth materials, various methods of chemical modification have been applied to increase the uptake of negatively charged anionic dyes. The adsorbents used include organo-attapulgite for the removal of Congo red [12]; organo-attapulgite and organo-smectite for the removal of brilliant blue [13]; and organo-zeolite for the removal of reactive red and reactive blue [14]. More interestingly, hen feather was proposed as a potential

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adsorbent for the removal of Congo red from wastewater [15]. Competitive sorption of anionic and cationic dyes onto cetylpyridinium-modified MMT was conducted [16], but detailed mechanism was not provided. Studies were also conducted for MO sorption on synthetic mesoporous silica containing cetyltrimethylammonium [17], again, no mechanism of MO uptake was speculated. Hydrogen bonding interaction was speculated to be operative between MO species and raw bentonite surface, but the analysis of thermodynamic parameters suggested that the uptake of MO on raw bentonite was mainly physical [10].

Several new or novel Gemini cationic surfactants were prepared and used to modify MMT or bentonite to enhance the removal of MO [18,19]. However, under alkaline conditions, the ester groups in the surfactant molecule are susceptible to hydrolysis and the removal rate of MO by the surfactant-modified bentonite decreased rapidly [19].

Zeolite is a group of hydrated aluminosilicates with a framework structure consisting of a network of interconnected tunnels and cages. The unique microporous structure and large isometric substitution lead to its several excellent properties, such as selective adsorption and ion exchange [20,21]. It is abundant on the surface of the Earth and is chemically stable. Hence, zeolite is commonly modified with surface functional groups to increase its uptake and removal of organic pollutants [22,23]. However, its application in dyestuff wastewater treatment is limited. The MO sorption increased to 22–24 mg/g for three synthetic zeolites after being modified by hexadecyltrimethylammonium (HDTMA) [24]. Ion exchange and electrostatic interactions were attributed to MO sorption onto those zeolites, although detailed experimental data to support the claim was missing.

Ionic liquid (IL) is an organic salt composed of organic macromolecules and inorganic anions. Recently, IL has been valued as a green solvent for organic synthesis [25]. Compared with traditional organic solvents, IL possesses unique properties, for example, non-volatility, low vapor pressure, and remarkable stability in a large temperature range. These unique properties make it an attractive alternative to volatile organic solvents [26]. Certain types of IL have strong affinity for MMT and zeolites, and thus could be used as modifiers to enhance the removal of anionic and organic contaminants from water. Furthermore, higher amount of IL modification would result in better contaminant removal [27].

Most of the studies on utilization of ionic-liquid-crafted zeolite (ILCZ) were focused on removal of chromate. Removal of anionic dyes using ILCZ has not been reported. This study focused on the removal of anionic dyes from solution by ILCZ, using MO as an example, under different physical and chemical conditions. The results could be extended to industrial applications at a larger scale once successfully demonstrated.

2. Materials and methods

2.1. Materials

The zeolite was obtained from the St. Cloud Mine in Winston, NM, USA. It contains 74% clinoptilolite, 10% quartz, 10% feldspar, and 5% other minerals [28], and has an external specific surface area (SSA) of 15.7 m²/g determined by N₂ adsorption, a total cation exchange capacity (TCEC) of 800 mmol_c/kg, and an external cation exchange capacity (ECEC) of 110 mmol_c/kg, with major exchangeable cations as Ca²⁺ and K⁺ [29]. The zeolite was used as received for surface modification by IL and subsequent experiments on MO removal under varying physical and chemical conditions.

The IL used was 1-hexadecyl-3-methylimidazolium chloride monohydrate (CAS#: 61546-01-8) with a molecular formula of C₂₀H₄₁ClN₂O, and formula mass of 361.01 g/mol. The molecular formula of MO (CAS #: 547-58-0) is C₁₄H₁₄N₃SO₃Na with a formula mass

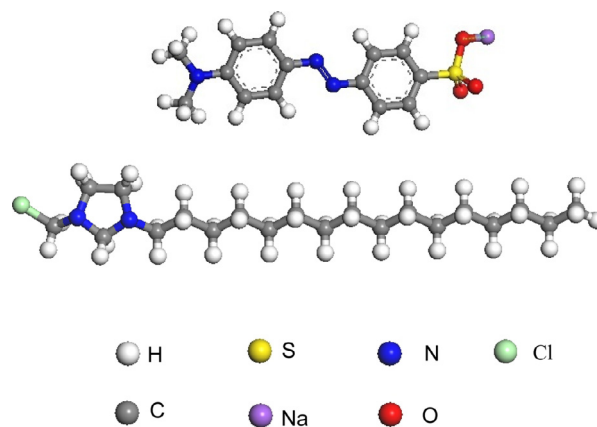


Fig. 1. Structures of methyl orange (top) and ionic liquid (bottom).

of 327.33 g/mol (Fig. 1). Both were purchased from Acros and were used as received.

2.2. Modification of zeolite by IL

Based on the ECEC, the zeolite was modified by IL to 1.0 and 2.0 ECEC to achieve a monolayer and bilayer IL surface coverage. The modification was made by mixing 200 mL of 15 or 30 mmol/L IL solution and 30 g of raw zeolite at room temperature at 150 rpm for 24 h. After centrifugation at 4500 rpm for 20 min, the supernatant was removed and analyzed for the equilibrium IL concentration by a UV–vis method. The counterion chloride concentration was analyzed by ion chromatography (IC). The mixture was washed twice, each with 180 mL of deionized water, and the equilibrium solution concentration of each wash was analyzed for IL and Cl⁻. The modified zeolite was allowed to air dry. For the ILCZ treated to 1.0 and 2.0 ECEC, the final IL loadings were 97 ± 4 and 190 ± 0.5 mmol/kg, respectively, in comparison to the ECEC of 110 mmol_c/kg. Meanwhile, the Cl⁻ loadings were 35 ± 1 and 85 ± 3 mmol/kg, respectively, for the ILCZ treated to 1.0 and 2.0 ECEC. These values suggested an almost complete bilayer formation of IL on the zeolite at 2.0 ECEC and admicelle formation of IL on the zeolite at 1.0 ECEC.

2.3. Batch study on MO removal

For the MO sorption study, 20 mL of MO solution was combined with 1.0 g ILCZ treated to 1.0 ECEC or 0.5 g ILCZ treated to 2.0 ECEC in a 50 mL centrifuge tube. For the isotherm study, the initial MO solution concentrations varied from 0 to 3.0 mmol/L. The kinetic study of MO sorption was conducted at initial concentrations of 1.8 and 3.0 mmol/L for ILCZ treated to 1.0 and 2.0 ECEC, respectively. For MO removal under different pH conditions, the initial MO concentrations were fixed at 1.8 and 3.0 mmol/L for ILCZ treated to 1.0 and 2.0 ECEC, respectively. The final solution pH was adjusted to 2–11 using 1.0 M HCl or NaOH. The same initial MO concentrations used in the kinetic and pH batch studies were also used for the ionic strength tests. The ionic strength of the solution was adjusted to 0.001–0.01 mmol/L using NaNO₃, Na₂SO₄, and NaHPO₄ to assess the effect of different types of anions on MO removal.

The mixtures of ILCZ and MO solution were shaken at room temperature at 150 rpm for 24 h, except for the kinetic study in which mixtures were shaken from 0.1 to 24 h. At the end of the shaking period, the mixtures were centrifuged at 4500 rpm for 20 min. Then, the supernatant solutions were analyzed for equilibrium MO concentration using a UV/VIS spectrophotometer. The MO removal was determined from the difference between the initial and final solution concentrations. All experiments were run in duplicate.

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