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Sorption of acid dye by surfactant modificated natural zeolites

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ABSTRACT

The adsorption of Acid Red 18 (AR18) by a natural zeolite (NZ) and its surfactant modified form (SMNZ) was investigated. The effects of initial dye concentration, contact time and adsorbent dose on the removal of AR18 were examined. Sorption kinetic was evaluated using the pseudo-second order, Elovich and Lagergren's first-order models. The equilibrium was analyzed by Freundlich, Langmuir, and Dubinin–Radushkevich models. The pseudo-second order kinetic model was found to agree well with the experimental data. The Langmuir isotherm was found to best represent the sorption data. The capacities of SMNZ and NZ for AR18 were found 20.42 and 1.17 mg/g, respectively. SMNZ could be a useful sorbent for the removal of AR18 from aqueous solutions.

1. Introduction

Due to the toxicity of dye effluents, their discharge to the environment, especially to water system, has becomes a major concern worldwide. These dyes are usually originated from industries such as dyestuff manufacturing, textiles, printing and dyeing. They can consume the dissolved oxygen content of water bodies which is needed for aquatic life. Some of them have a direct toxicity effect on microbial populations and even can be carcinogen or toxic to the mammals [1,2].

The structural varieties of dyes can fall into either the cationic, non-ionic or anionic types. Among these types, the anionic dyes include direct, acid and reactive dyes [3]. Brightly colored water-soluble reactive and acid dyes are the most problematic dyes, which tend to pass through the conventional treatment systems unaffected easily [4]. In addition, the presence of the dyes in water bodies can decreases the rate of photosynthetic process [5].

Nowadays, several treatment processes are used in the removal of dyes from aqueous solutions including: precipitation, ultrafiltration, ion exchange, phytoextraction, electrodialysis and reverse osmosis. However, the adsorption process is preferred for the removal of these pollutants due to easy handling and high removal performance [2,6–8]. On the other hand, the efficacy of the adsorption process and its economy are limited by the physicochemical characteristics and the cost of the adsorbent [9]. In this context, several researchers have studied the removal of dyes from mono-component solutions using low-cost adsorbents with inorganic origin such as clay materials. Clay minerals, as low cost natural adsorbents, are natural scavenger of pollutants from water through adsorption mechanisms [10] and ion exchange process [11]. Natural zeolites are good adsorbent for the dyes [12,13] and they have already found many applications because of their high cation-exchange capacity and surface area. They are mainly composed of aluminosilicates with a three dimensional framework structure bearing AlO_4 and SiO_4 tetrahedra that are linked to each other by sharing all of their oxygens to form interconnected cages and channels containing mobile water molecules and alkalis and/or alkaline earths [14]. Nowadays, functionalization of zeolites is a very promising approach for designing materials with novel surface properties and making them more suitable for specific applications [15,16].The common surface functionalization of these materials is via adsorption of cationic surfactants [17]. The natural zeolites (NZ) are most common inorganic materials used for surface modification, because they possess permanent negative charges in their crystal structure, making them suitable for this kind of modification. Sorption of a cationic surfactant onto a negatively charged surface involves both cation exchange and hydrophobic bonding mechanisms [18]. Surfactant modified natural zeolite (SMNZ) can remove organic compounds and oxyanions from water. Partitioning is responsible for organic sorption by SMNZ [19]. The capacity of zeolites for the dye sorption is limited

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and in many of studies their modification have been reported by surfactants, such as hexadecyltrimethylammonium (HTAB) [20], tetramethylammonium(TMA) [21], cetylpyridiniumbromide (CPB), and octadecyldimethylbenzyl (ODMBA) [22] to improve their sorption capacities. SMNZ has been used for the removal of various pollutants from aqueous solutions, such as phosphorous [23], humic acid [24], and heavy metals [25,26]. However, SMNZ is used as a sorbent for removal of dyes from aqueous solutions. For example it has been used for the removal of Congo Red [13], reactive dyes [27], Remazol Brillant Blue R and Remazol Yellow [28] from aqueous solutions. It seems that further batch studies are needed to investigate the capacity of SMNZ for the removal of dyes from aqueous environments.

A batch equilibrium adsorption study can be carried out to assess the adsorption capacity of a given sorbent for the sorption of an adsorbate. The equilibrium of the sorption of a material at a surface can be described by adsorption isotherms which are often used as empirical models [29]. An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium condition and a constant temperature. The adsorption isotherm is very important to design the adsorption systems. Isotherm models are obtained from measured data by means of regression analysis. The most frequently used isotherms are the Freundlich and Langmuir models [30]. Except for adsorption capacity, kinetic performance of a given adsorbent is also of a great importance in the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established and one can know the scale of an adsorption apparatus based on the kinetic information [31].

This study aims to examine the adsorption capacities of locally-derived sorbents, SMNZ and NZ (obtained from natural mines in the southeast Semnan, a city in north eastern Iran) for the sorption of Acid Red 18 (AR18) from aqueous solutions. The sorption of AR18 onto SMNZ was studied by performing batch kinetic and equilibrium experiments. The experimental data were analyzed using the Freundlich, Langmuir and Dubinin–Radushkevich isotherm models. The kinetic data were also analyzed to predict the constant rate of adsorption using three common kinetic models: pseudo-second order, Elovich and Lagergren first-order models. The effects of parameters such as dye concentration, pH and dosage of sorbent were analyzed for the purpose of understanding the adsorption behavior of dye onto SMNZ.

2. Experimental

2.1. Sorbent preparation

Local natural zeolitefrom the mines in the southeast of Semnan (a province in northeastern Iran) was used to prepare modified sorbent. First of all the zeolite was crushed and passed through a series of sieves (50 and 70 U.S. standard mesh sizes). In order to remove dirt and dust particles, zeolite samples were washed in tap water and then twicewith distilled water. To remove the dissolved salts and impurities, the samples were placed in contact with distilled water for 1 h and then were washed with distilled water and dried at 200 C in an oven overnight [26,32,33]. The dried samples were sieved using metal sieves and a mixture of the residuals on 50 and 70 sieves was kept in a bottle and used for further investigation. The average adsorbent particle size was 0.27 mm.

To improve the cation exchange capacity of zeolite samples, a solution of sodium chloride salt was used to saturate the exchange sites with sodium ions, before modifying the surface of zeolites with surfactant. For this purpose, a one molar solution of sodium chloride was prepared and a dosage of 100 g/L of zeolites was contacted with the solution and shaked with speed of 170 rpm for 48 h. Because the

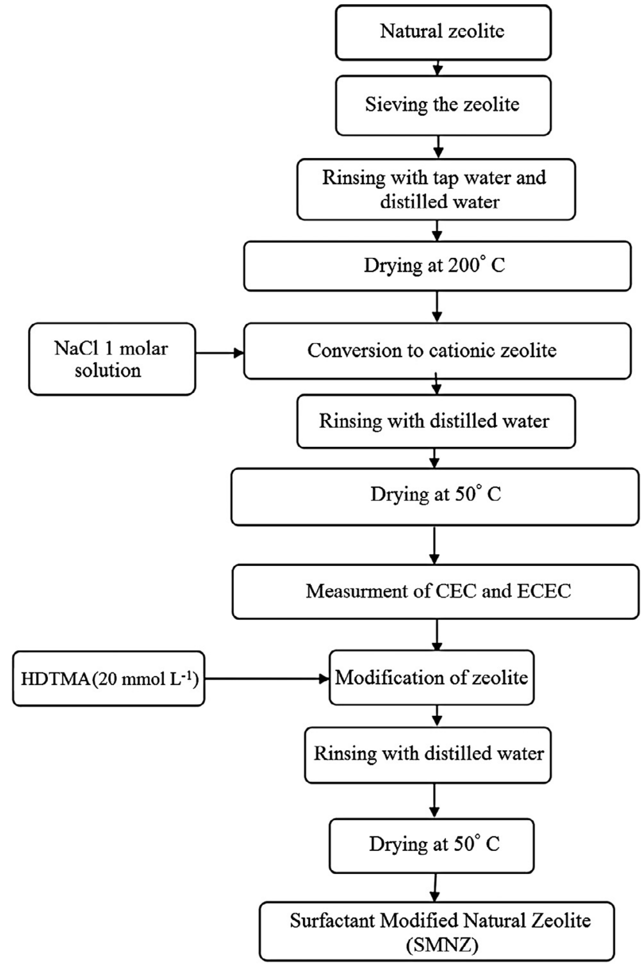

Fig. 1. Preparation of SMNZ.

chloride ions may affect the properties of modified zeolite, samples were washed with distilled water to remove residual chloride ions. The wash waste solution was analyzed for the presence of chloride ion using the argentometric titration method in order to ensure the removal of chloride ions [17,20,34].

The improved-cation-exchange-capacity samples were dried at 50 C in an oven overnight and used as natural zeolite (NZ) in the adsorption experiments.

Total cation exchange capacity (CEC) and the external CEC (ECEC) of zeolites were measured using Haggerty and Bowman [35] method.

Surfactant modified natural zeolite (SMNZ) affords a hydrophobic environment for the partitioning of organic molecules with low polarity and high molecular weight [36]. The preparation of SMNZ was carried out according to Fig. 1. Hexadecyltrimethylammonium bromide (HTAB) supplied by Merck with a concentration of 20 mmol/L was used for the preparation of SMNZ. 10 g of prepared cationic zeolite samples with 100 mL of HTAB solution were added to a 125 mL polyethylene bottle. The dispersions were shaked at room temperature by a mechanic shaker for 24 h followed by washing with distilled water. Therefore, the modified zeolite samples were dried at 50 C in an oven overnight [20]. In a study conducted by Ghadiri et al. [32], the modification of a clinoptilolite-type zeolite with a concentration of 20 mmol/L of HTAB provides the highest sorption capacity for the removal of MTBE from aqueous solutions.

The properties of zeolites were investigated by X-ray fluorescence (XRF) (PW 2404 Philips Holland) and X-ray diffractometer (X'Pert MPD Philips Holland) operated at 40 kV and 40 mA. The XRD