Iran. J. Environ. Health. Sci. Eng., 2008, Vol. 5, No. 1, pp. 73-77

REMOVAL OF CHROMATE ION FROM CONTAMINATED SYNTHETIC WATER USING MCM-41/ZSM-5 COMPOSITE

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Received 21 September 2007; revised 20 November 2007; accepted 28 December 2007

ABSTRACT

In the present study removal of chromate anion (CrO_4^{2-}) from a synthetic aqueous solution by a synthesized MCM-41/ZSM-5 composite and its modified form with the anionic surfactant of hexadecyl-teri methyl ammonium bromide; (surfactant modified composite) was investigated. According to the data obtained from batch test of MCM-41/ZSM-5 composite and surfactant modified composite, it is obvious that modification of the composite with anionic surfactant improves its affinity toward the oxyanion (917mL/g for MCM-41/ZSM-5 composite in comparison to 1870mL/g for surfactant modified composite). It was concluded that sorption capacity and selectivity of the composite will be remarkly improve toward chromate anion by modification of its surface by a surfactant; therefore surfactant modified composite is a suitable candidate for removal of chromate anion from contaminated solutions.

Key words: Chromate, MCM-41/ZSM-5 composite, wastewater

INTRODUCTION

The increasing contamination of urban and industrial wastewater by toxic metal ions is a worrying environmental problem. These inorganic micro-pollutants are of considerable concern because they are non-biodegradable, highly toxic and have a probable carcinogenic effect (Modani *et al.*, 1996). In view of their high toxicity for human health, heavy metal concentrations in wastewater are restricted by strict standards. The risk of exposure to toxic oxy-anions in groundwater is a worldwide rising environmental risk.

Among these anions, chromate is particularly hazardous. Chromate is one such toxic ion that requires considerable attention (Adam and Pribil, 1974). The chromate (CrO_4^{2-}) oxyanion is soluble in aqueous systems and is readily transported in ground water and the EPA maximum contaminant level for Chromium in drinking water is 0.1 parts per million (Sadaoui, 1998). Aqueous solutions of chromate (CrO_4^{2-}) are known to undergo oligomerization reactions upon acidification. These kinds of polymerization processes are in general very common in aqueous solutions as they apply for the precipitation mechanism of hydroxides and oxides at basic pH conditions (Stern, 2000).

The traditional techniques for the removal of metal ions from aqueous effluents; such as lime precipitation are incapable of reducing concentration to the levels required by standards (Chai *et al.*, 1997). Nowadays, utilization of ion-exchange process to clean up the contaminated solutions with toxic ions is attractive for scientists. Adsorption of toxic species on solid surfaces is considered to be an effective method for improving the environment. These methods have been aimed at searching for effective adsorbents or the development of geochemical models of chromate distribution. Conventional porous solids, such as coconut coir, zeolite, and clay minerals, modified with surfactants have been applied to the removal

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of chromate. These composite materials, with ill-defined structures, showed low absorption capacities. The required properties of the ideal adsorbent are uniformLy accessible pores, high density of adsorption sites, and environmental adaptability. However, natural minerals and biomass do not satisfy these geometric conditions (Krishna *et al.*, 2001).

A decade has passed since the discovery of a family of novel mesoporous molecular sieves synthesized with the aid of micelle templates (Inagaki *et al.*,1993). A huge number of researches have been devoted to the materials in this new category. The pore structure is unique, as they form well-ordered periodic structures, and, in addition, the pore size is controllable by varying the template molecule (Ying *et al.*, 1999). The characteristics of mesoporous molecular sieves are attractive to researchers seeking adsorbents of low concentration ions in the environment. Because the efficient adsorption of a certain target ion is not expected on silica surfaces, the strategy of functionalization of the surface must be designed for oxyanion adsorption (Liu *et al*; 2000). In the present study, possible sorption and removal of chromate anions (CrO_4^{2-}) from contaminated solutions was studied by using MCM-41/ZSM-5 composite (MZC) and the surfactant hexadecyl-teri methyl ammonium bromide (HDTMABr) surfactant modified composite (SMC).

MATERIALS AND METHODS

The chemicals used in this work were selected from analytical grade materials (Fluka). Synthetic contaminated water was used. Also, The MCM-41/ZSM-5 composite MZC was synthesized according to a procedure described in the literature (Huang *et al.*, 2000). and was used to study the sorption process. To synthesize the composite, template agent solution of tetra propyl ammonium bromide (TPABr) (3.55g TPABr dissolved in 9mL of deionized water) was first mixed with 16g of glass water (7.4% Na_2O, 25.4% SiO_2, 67.2% H_2O; w%) and $NaAlO_2$ solution (0.36g sodium aluminate dissolved in 9mL of water). The composite were characterized by mean of a low angel x-ray diffractometer (XRD-Philips PW-1800, Cu Kα, 40kV). To perform sorption

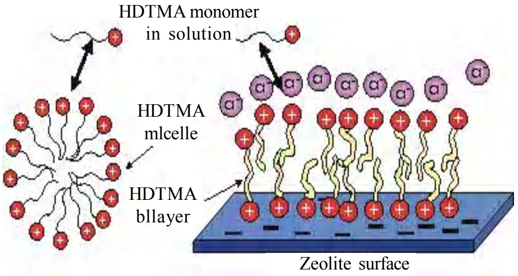

Fig. 1: Schematic diagram of modification of a zeolite surface by surfactant (Ranck *et al.*, 2005)

experiments, the SMC was then prepared by treating the synthesized powder with HDTMA-Br anionic surfactant solution (Ranck *et al.*, 2005). To do this, 10g of the composite powder was reacted with 100mL of a 0.17M solution of HDTMA-Br. The mixture was shaken at 25ºC for 24h; the resulted modified composite was then filtered, rinsed with 500mL of deionized water and air dried overnight. To investigate the selectivity of SMC toward chromate anion and in order to test its capability for the anion removal, aqueous synthetic solutions with metal concentration in the range of 2.5×10^{-3} to 2×10^{-2} moL/dm^3 was used to test the sorbents under static (batch operation) and dynamic (column operation) conditions. For batch tests, 0.2g of MZC or SMC sorbents was shaken with 25mL of the potassium chromate solutions at 25°C for 24h. The liquid phase were separated by centrifuging at 4000rpm for 20min, chromium concentration in liquid phase was measured by an inductively coupled plasma-atomic emission spectrometer (ICP-AE; Liberty 150 AX Turbo). To evaluate the sorbents selectivity toward chromate, distribution coefficient (K_d) was calculated using the following equation:

$$K_d = (C_i-C_f) / C_f\times(V/m)$$

Where:

C_i and C_f are the initial and the final concentration of cations respectively, m is the weight of sample (exchanger) in grams and V is the volume of solution in milliliters.

To evaluate the efficiency of the MZC and SMC sorbents in dynamic condition, breakthrough curves were plotted by performing column tests. To do this, 0.2g of the sorbent powder was loaded into a glass column with internal diameter of 1 cm which was equipped to a peristaltic pump to adjust solution flow rate. 0.01M solution of potassium chromate was passed through the column with a flow rate of 0.4mL/min. Series of 5mL portions of effluent were collected to measure the chromate concentration the solution. Breakthrough curves were obtain by plotting of the C/C_o ratio versus V (mL), in which C and C_o are final and initial concentration of chromate in solution, respectively, and V is the cumulative volume of solution in mL.

RESULTS

The developed composite (MZC) was characterized by mean of instrumental analysis using XRD technique. The XRD pattern of the MZC sample, which was synthesized according to the two step crystallization route, as well as reference composite (Huang *et al.*, 2000) are illustrated in Fig. 2 and Fig. 3 respectively. The composite were characterized by using a low angel x-ray diffractometer (XRD-Philips PW-1800, Cu Kα, 40kV). Since the contaminant concentration is one of the key parameters of the ion exchange investigations for environmental purposes and in order to consider the influence of chromate ion concentration on behavior of the composite sorbents, the effect of concentration of the oxyanion on its distribution coefficients (K_d,dm^3/g) on the MZC and SMC sorbents were examined. The numerical data, which were resulted from sorption experiments in a batch condition is presented in Table 1 and illustrated in Figs. 4 and 5 respectively.

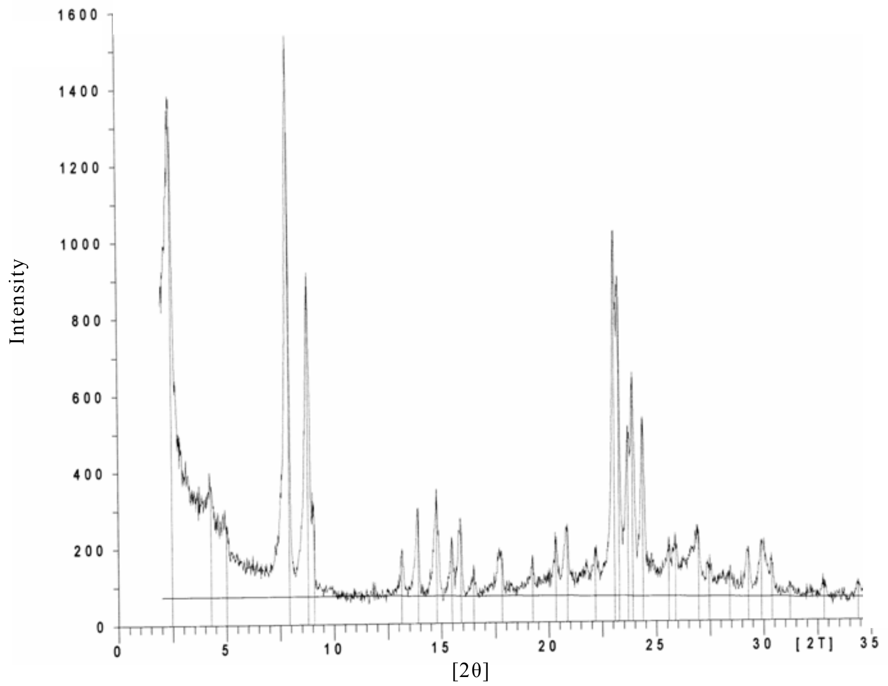

Fig. 2: XRD pattern of the synthesized MCM-41/ZSM-5 composite

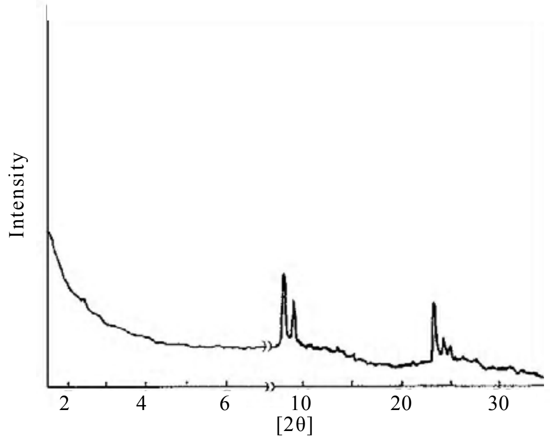

Fig. 3: XRD pattern of the reference MCM-41/ZSM-5 composite (Huang *et al.*, 2000)

To evaluate capability of the developed composite sorbents for industrial applications, it was necessary to determine their uptake behavior in a dynamic (continues) condition. To do this, some sort of column tests have been performed. The results obtained from column experiments, which are the breakthrough curves, are shown in Figs. 6 and 7.

Table 1: Effect of CrO_4^{2-} concentration (mg/L) on the distribution coefficient K_d(mL/g)

Test No.	MZC		SMZ	
	CrO_4^{2-} (mg/L)	K_d (mL/g)	CrO_4^{2-} (mg/L)	K_d (mL/g)
1	100	917	100	1870
2	200	907	200	1867
3	500	895	500	1844
4	1000	887	1000	1826

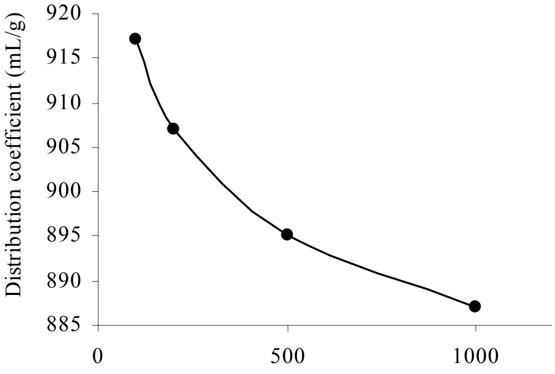

Fig. 4: Dependency of distribution coefficient of the synthesized MCM-41/ZSM-5 composite for removal of chromate anion

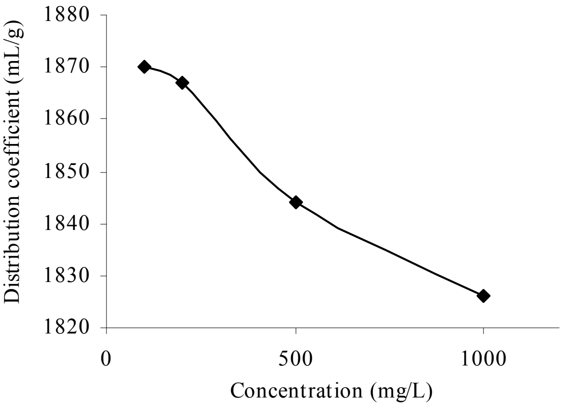

Fig. 5: Dependency of distribution coefficient of the modified synthesized MCM-41/ZSM-5 composite for removal of chromate anion

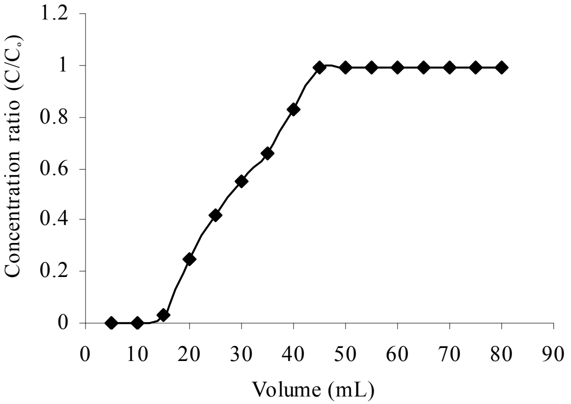

Fig. 6: Breakthrough curve of chromate anion on the MCM-41/ZSM-5 composite

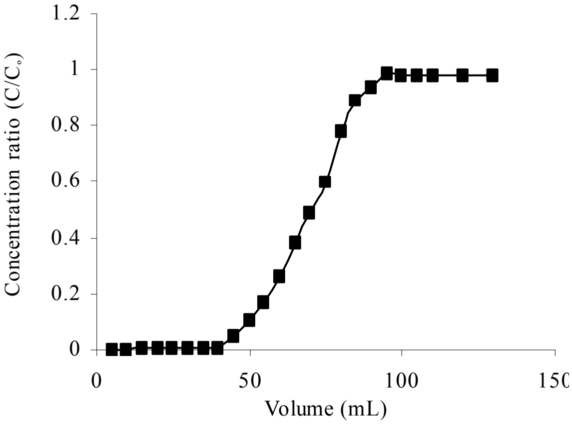

Fig .7: Breakthrough curve of chromate anion on the modified MCM-41/ZSM-5 composite

DISCUSSION

Comparing of the patterns reveal the composite was successfully synthesized. Sharp peak at 2 theta lower than 2 is the characteristic peak of MCM-41 mesopore (Huang *et al.*, 2000).

Based on the data, sorbents selectivity toward the anion will decrease by increasing of the ingoing anion concentration. This can be considered as a result of the nature of K_d formula (Kazemian *et al.*, 2001), which is imply that the sorbents show higher affinity to the anion at lower concentration. This behavior is promising for environmental application of sorbents, where removal of trace concentration is a big deal for scientists working in the field of liquid waste management. According to the data obtained from batch test of MZC and SMC, it is obvious that modification of the composite with anionic surfactant improves its affinity toward the oxyanion (917mL/g for MZC in comparison to 1870mL/g for SMC). Based on the curves, breaking point volume of SMC is 3 times higher than of MZC, (45mL for SMC in comparison to 15mL for MZC). This implies that sorption capacity of the composite will be remarkly improve by modification of its surface by a surfactant. This finding reveals that the sorption mechanism is based on a surface phenomenon.

A composite (MCM-41/ZSM-5) material based on a micropore zeolite (ZSM-5) and a mesopore (MCM-41) has been successfully synthesized according to a two step crystallization procedure. Chromate removal tests, which have been carried out in batch and column condition revealed that the synthesized composite; MZC, affinity toward the chromate oxyanion was not considerable, whereas its surfactant modified form; SMC, shows remarkable selectivity toward chromate anion. Sorption tests, which carried out under dynamic condition (column test), showed promising results for application of the SMC at larger scales. Since any other patented or published experiences was not found regarding chromate anion sorption on the MZC and SMC worldwide; further investigation is required to optimize the procedure. In this concern it is necessary to consider the effect of some other parameters such as media pH, reaction temperature, sorbents particle size, stream flow rat for column test, etc.

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