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Synthesis and characterization of poly (AAm-co-AAc)/NaA nanocomposite and removal of methylene blue with it

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Abstract

The nanocomposites of poly (Acryl amide-co-Acrylic acid) with different contents of NaA zeolite were prepared using ammonium persulfate as an initiator and N, N′-methylene bisacrylamide as the crosslinker. The morphology was characterized by SEM and the structure of nanocomposite materials was studied with XRD and FT-IR that showed the interaction between porous materials and poly (AAm-co-Aac). The adsorption behaviors of methylene blue were investigated for nanocomposites. It was shown that poly (AAm-co-AAc)/NaA nanocomposites have higher adsorption than NaA and poly (AAm-co-AAc) alone. This effect was attributed to good interaction between the hydroxyl group in porous materials and carboxylic group in poly (AAm-co-AAc) with methylene blue.

Keywords: Nanocomposites; Poly (Acryl amide-co-Acrylic acid); NaA zeolite; Adsorption; Methylene blue

1. Introduction

Zeolites are crystalline aluminosilicates with uniform micrometer-sized pores [1]. Their unique frameworks and high specific surface areas make them, depending on composition and porous geometry, broadly applicable in petrochemical processes, in fine chemical and pharmaceutical production [2, 3], in contamination abatement [4], in sensors [5, 6], and in optoelectronic materials [7]. Among the zeolites, Linde Type A (LTA), has been the objective of many investigations/applications due to its long history. Zeolite A with sodium cations, denoted as NaA, has a formula of $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]^{-}.27H_2O$, and contains cages with orthogonal 3-D oriented apertures of approximately 0.4 nm. The pore dimension is changed to 0.45 or 0.30 nm, when the zeolite is ion exchanged with Ca^{2+} or K^{+}, respectively [8].

In addition, NaA zeolite, with high aluminum content, has high affinity for water in nature, which was reported to be extremely effective for dehydration of alcohol/water mixtures by pervaporation [9-11]. Therefore, more and more interest has been focused on synthesis and application of NaA zeolite membrane in the last 10 years [12–18]. Moreover, over the past several decades, polymeric hydrogels play an important role in the treatment of wastewater. Because the super absorbent hydrogels have ionic functional groups, they can absorb and trap

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ionic dyes such as MB From wastewaters [19]. But these polymers have several limitations and always exhibit mechanically week, brittle properties and low porosity [20]. Thus, many potential applications of conventional polymeric hydrogels have been restricted or abandoned because of their limitations. Incorporation of these mineral powders not only reduces costs but also improves the properties (such as swelling ability, gel strength, mechanical and thermal stability) [21].

In this study we prepared the novel superabsorbent hydrogel nanocomposites by using of the polyacrylamide (PAM), acrylic acid (AA) and MCM-41. These composites have many advantages such as high stability and high porosity. The adsorption and desorption behavior of methylene blue were investigated for nanocomposites.

2. Experimental

The optimum molar ratio of initial materials for preparation of poly (AAm-co-AAc) considered at prior work in our laboratory [22]. Several nanocomposites with different amount of NaA zeolite were prepared by radical graft copolymerization. Typical preparation conditions for samples are as follows:

At first, Potassium acrylate was prepared by partially neutralizing a diluted acrylic acid solution with a predetermined amount of 50 wt % aqueous potassium hydroxide solution which was added drop wise in an ice bath. Then, the cross-linker (N, N′-methylene bis acryl amide) was carefully added to the acryl amide solution. A given amount NaA zeolite (0.15, 0.30, 0.45, 0.60 g) that ultrasound for 1h before use for getting nano size was slowly added to stirring monomer mixture. Then the first neutralized solution was added to it. The suspension obtained was mixed 30 minutes by a 300 rpm magnetic mixer. In the next step, TMED and APS were added to the pore material-polymer mixed solution. Then the products were removed from the beaker, cut to small pieces and dried 72 to 96 hours in laboratory conditions.

Then a weighed quantity of dry hybrid hydrogel (0.2 g) with different composition was immersed in enough methylene blue (50 μg mL^{-1}) and kept at 37 ^{o}C. The amount of MB adsorbed was measured spectrophotometrically (λ: 661.6 nm) in periodically taken solution samples and again placed in the same vessel so that the liquid volume was kept constant. The removal efficiency (RE %) of the dye by the hydrogels with different composition was calculated by Eq. (1) :

$$RE\% = (C_o - C/C_o) \times 100 \qquad (1)$$

That C_o and C are the initial and equilibrium concentration of the MB dye solution, respectively.

3. Results and discussion

Fig. 1a shows FT-IR spectra in the range of 500 to 4000 cm^{-1} for poly (AAm-co-AAc). The FT-IR spectra of the dried hydrogels show the broad band in 3439 cm^{-1} is due to N-H groups of polyacrylamide and the peak at 1700 cm^{-1} represents the carbonyl group. There is a shoulder at 1715 cm^{-1} which corresponds to the carbonyl group of polyacrylate. Also we can see two bonds at 1384 and 1570 cm^{-1} related to COO^- group in polyacrylate and the peaks at 1456, 2953 cm^{-1} represent the C-N and C-H bonding, respectively . poly (AAm-co-AAc)/NaA show the peaks of carbonyl shifted to 1682 cm^{-1} and the intensity of the peaks at 3400 cm^{-1} correspond to N-H decreased and shifted to lower frequency . It may be because of the formation of hydrogen bonding between COOH, NH_2 of the copolymer and hydroxyl groups of Al-OH and Si-OH in pore materials. Also we can see two bands at about 1120 cm^{-1} due to Si-O and 480 cm^{-1} related to Al-OH in the composites (Fig. 1a).X-ray diffraction patterns of NaA, poly (AAm-co-AAc)/NaA are shown in Fig. 2a, 2b, respectively.

Decrease of intensity corresponds to covering particles with polymer.SEM images of the NaA zeolite and poly (AAm-co-AAc)/NaA zeolite are shown in Fig. 3a, 3b, respectively. There is a considerable change between two samples. From the micrographs, it was found that the NaA was dispersed in the polymer network. Several areas show fine network structure .It means that NaA has good collaborate with poly (AAm-co-AAc).

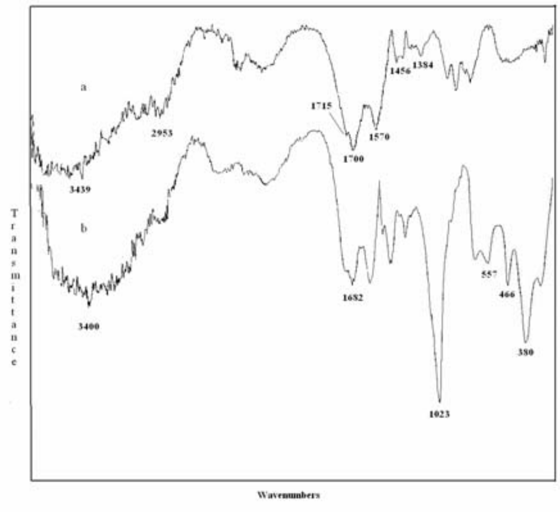

Fig. 1. FT-IR spectrum of poly (AAm-co-AAc) (a), poly (AAm-co-AAc)/NaA zeolite (b).

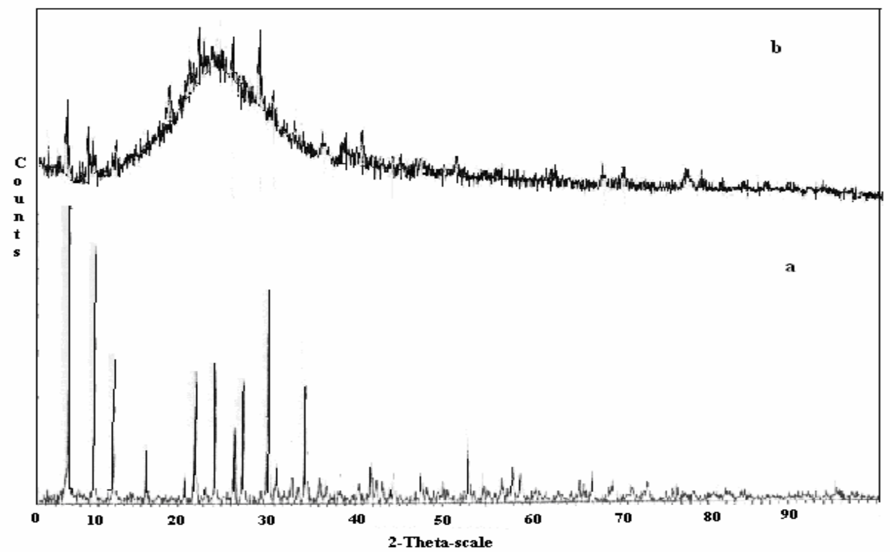

Fig. 2. X-ray diffraction patterns of NaA (a), poly (AAm-co-AAc)/NaA zeolite (b).

3.1. Adsorption of methylen blue

Fig. 4a shows the removal effect of methylene blue by NaA, poly (AAm-co-AAc) and poly (AAm-co-AAc)/NaA composites, respectively. The maximum adsorption is about 12% of MB from aqueous solution by poly (AAm-co-AAc)/NaA. Also, when we use of poly (AAm-co-AAc) alone, maximum adsorption is about 82%. Removal effect of MB increased when the NaA added to poly (AAm-co-AAc) up to 95%. Result (Fig. 4b) indicates with using higher content of NaA from 0.15g to 0.6g in nanocomposites, it has not adsorbed more MB as expected. These results confirmed that both porous materials (NaA zeolite and clinoptilolite) and poly (AAm-co-AAc) play a critical role in MB adsorption. We know the poly (AAm-co-AAc) does not adsorbed cationic dye from solution, since poly acryl amide is non ionic polymer [23]. Therefore, we interred polyacrylic acid to it and increased the ionic groups (COO^-) for adsorption of cationic dye.

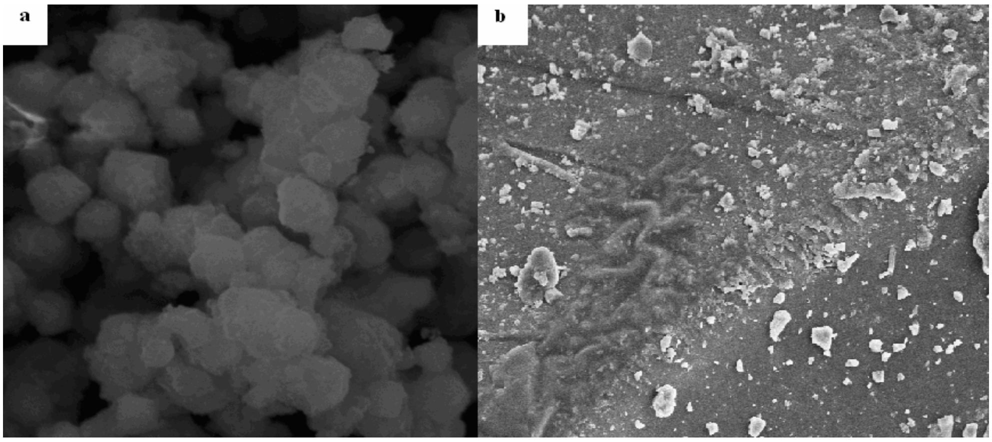

Fig. 3. SEM images of NaA zeolite (a) and poly (AAm-co-AAc)/NaA zeolite (b).

Hence, the cationic dye may be interacted to the NaA and clinoptilolite by different modes: 1. the cations on zeolite and clinoptilolite may exchange with MB cations from solutions.2. The adsorption is on through porous zeolite without any ion-exchange3. The dye adsorbs on the surface of porous materials [24].

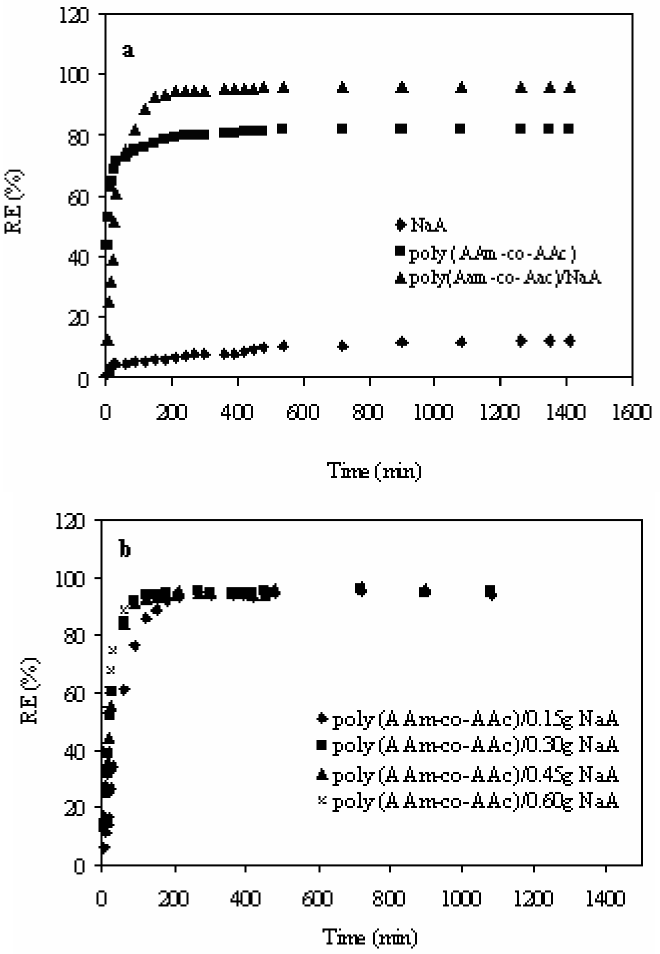

Fig. 4. The effect of NaA zeolite in polymer network on removal effect of MB (a) and the effect of NaA zeolite content on removal effect of MB (b).

4. Conclusion

The nanocomposite from poly (AAm-co-AAc) with NaA zeolite was prepared. The SEM shows that NaA dispersed on poly (AAm-co-AAc) matrix and XRD shows interaction between NaA and poly (AAm-co-AAc). FT-IR spectroscopy shows interaction between carboxylic group in polymer and hydroxyl group of NaA. Hence, efficiency of these composites was considered for removal of methylene blue from water. The adsorption of MB increased with using of poly (AAm-co-AAc)/NaA, related to NaA and poly (AAm-co-AAc) alone. This improvement in the removal efficiency in nanocomposites may be due to the increase in the population of anion sites and porosity of composites which enhance the interactions between MB and composites.

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