

Magnetite nanoparticles activated coal fly ash zeolites with application in waste water remediation

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Abstract

In this study, fly ash zeolites (FAZ) were synthesized by a double stage fusion-hydrothermal treatment. Magnetite nanoparticles were added to FAZ between the two synthesis stages. The obtained nanocomposites (MNP-FAZ) and their parent FAZ were studied with respect to their surface characteristics and were tested for decontamination of polluted waters. The experimentally obtained equilibrium adsorption isotherms were described applying different computational models.

Keywords: Fly ash zeolites, Magnetite nanoparticles, Adsorption isotherms, Waste water remediation

1. Introduction

In the context of environmental protection and conservation of natural resources, zeolites are derived from waste aluminosilicates. Recently, many research efforts have been done on the utilization of coal fly ash (FA) converting it into zeolites due to their compositional similarities (Ahmaruzzaman). Generally, fly ash zeolites (FAZ) with excellent surface characteristics are synthesized by a double stage fusion-hydrothermal activation including high thermal stage prior to the hydrothermal treatment (Querol et al.). However, drawback of this synthesis manner is that magnetite from the raw FA undergoes thermal oxidation to hematite preventing the simultaneous presence of Fe^{2+/3+} ions into FAZ, which is otherwise important for their decontamination efficiency. Thus, prepared FAZ also suffer from the disruption of their magnetic activity, as the magnetic zeolite adsorbents are removed from decontaminated media by a simple magnetic process. The target of this study is to obtain FAZ taking advantages of the double stage synthesis but protecting the magnetic properties of the resultant materials by adding and finely distributing in its structural network of magnetite nanoparticles (MNP) at an interim step between the fusion and hydrothermal stages. It is expected that the magnetite activation of FAZ will facilitate the separation of their powders from decontaminated media.

2. Experimental

Mixtures of 5 g FA and 10 g NaOH were heated at 550 °C in Ni-crucibles. The products were grinded and spread into 100 ml distilled water. MNP were prepared by coprecipitation method of ferric and ferrous ion salts by a strong base (Mascolo et al.) In this synthesis, 0.01 mol FeCl₂·4H₂O and 0.02 mol FeCl₃·6H₂O were dissolved in 100 ml deionized water and added into a 250 ml three-neck flask kept at 298 K in a water bath. The reaction solution was stirred at 500 rpm under N₂ flow. Dissolved 0.8 mol NaOH in 100 ml deionized water was added, and stirring continued for 3 h, until final pH=12 was recorded. The suspension was decanted, washed, and the MNP were separated by a permanent magnet and dried at room temperature. MNP were added in 4 wt.% (MNP-FAZ1), 8 wt.% (MNP-FAZ2) and 12 wt.% (MNP-FAZ3) vs. the weight of the raw FA and dispersed into the zeolitization slurries by sonication for 15 min. The mixtures were hydrothermally activated for 4 h at 90 °C in closed vessels. The zeolite powders were separated by filtration, washed and dried at 105 °C. Nitrogen adsorption/desorption isotherms were measured at 77 K by a volumetric adsorption analyzer Tristar II 3020, Micromeritics. Samples were preliminary degassed in a set-up FlowPrep 60, Micromeritics, at 260 °C for 4 h under He flow. The adsorption behavior of FAZ was tested toward methylene blue (MB) as a model water contaminant. The experiments were performed by batch technique immersing 0.1000 g FAZ into 25 ml of MB solutions with varying concentration under magnetic stirring 100 rev⁻¹ at 25 °C. The optical adsorption (A) was measured after 24 h at λ=665 nm.

3. Results and Discussions

Parent FAZ and FAZ loaded by different amount of magnetite nanoparticles were characterized with respect to their surface properties (Table 1).

Table 1. Surface characteristics of FAZ

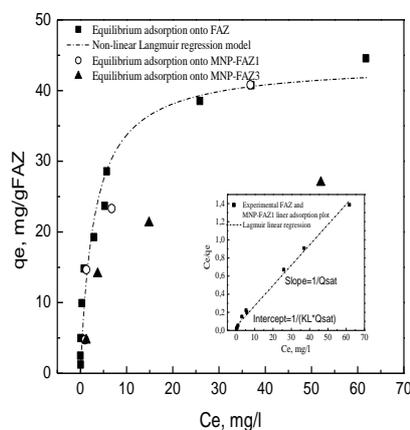
Surface parameter	FAZ	MNP-FAZ1	MNP-FAZ2	MNP-FAZ3
S_{BET} , m ² /g	486	264	207	137
V_{micro} , cm ³ /g	0.13	0.06	0.04	0.02
V_{meso} , cm ³ /g	0.17	0.19	0.16	0.17
V_{total} , cm ³ /g	0.31	0.25	0.21	0.20
d_{micro} , Å	13.94	13.49	12.82	11.32
d_{meso} , Å	41.79	49.34	49.75	61.79

S_{BET} -specific surface; V_{micro} , V_{meso} , V_{total} – internal volume described by micro and mesopores, and total pore volume, correspondingly; d_{micro} , d_{meso} – average micro and mesopore sizes.

Obviously, MNP loading of FAZ reduces S_{BET} values but exceeds mesoporosity, which is better pronounced for the sample containing the highest amount of magnetite nanoparticles (MNP-FAZ3). The experimental and model adsorption isotherms of MB onto FAZ, MNP-FAZ1 and MNP-FAZ3 are presented in Fig.1. The equilibrium adsorbed quantity q_e of MB on the zeolites was calculated as follow:

$$q_e = (C_{in} - C_e) V / m_s, \text{ mgMB/g FAZ}$$

Where: C_{in} is MB concentration in the stock solution, mg/l; C_e is the final MB concentration at the end of the adsorption, mg/l; V is the test solution volume, l; m_s is weight of the solids used in the adsorption, g.

**Figure 1.** Adsorption isotherms of MB on FAZ

The experimental results indicate that the MNP zeolite loading up to 8 wt.% does not affect significantly the adsorption ability of FAZ despite the lower specific surface parameter. Moreover, the adsorption isotherms of FAZ and MNP-FAZ1 overlap. However, the MB adsorption onto MNP-FAZ3 containing 12 wt % of magnetite nanoparticles is drastically reduced. The experimental adsorption isotherms were described mathematically by the most applied adsorption models, and the estimated parameters and the correlation coefficient R^2 are presented in Table 2. Comparative studies of linear and non-linear Langmuir model regression for description of the experimental equilibrium adsorption were performed.

Table 2. Model parameters of MB adsorption isotherms on FAZ and MNP-FAZ

Models	Parameters	
Langmuir linear $C_e/q_e = 1/K_L Q_{sat} + C_e/Q_{sat}$	Q_{sat} , mg/g	44.70
	K_L , l/mg	0.45
	R^2	0.993
Langmuir non-linear $q_e = \frac{Q_{sat} K_L C_e}{1 + K_L C_e}$	Q_{sat} , mg/g	43.88
	K_L , l/mg	0.33
	R^2	0.953
Freundlich non-linear $q_e = K_f C_e^{1/n}$	K_f , mg/g	14.62
	n	3.51
	R^2	0.977
Langmuir-Freundlich non-linear $q_e = \frac{Q_{sat} (K_L C_e)^n}{(K_L C_e)^n + 1}$	Q_{sat} , mg/g	65.95
	K_L , l/mg	0.28
	n	0.49
	R^2	0.992

Q_{sat} is the adsorption capacity of solids; K_L and K_f are the Langmuir and Freundlich isotherm constants, correspondingly; n is the index of heterogeneity.

According to R^2 values, the experimental adsorption is described the best by Langmuir linear and Langmuir-Freundlich non-linear regression models.

4. Conclusions

Coal ash zeolites activated by magnetite nanoparticles up to 8 wt. % are characterized by similar adsorption ability toward methylene blue as compared to the parent sample despite the reduction in the specific surface area.

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