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# Removal of phenolic compounds by adsorption on nano structured aluminosilicates

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ABSTRACT

Nano structured aluminosilicates with different concentration of Al and Si were synthesized by alkoxides precursors and sol–gel methods. The chemical analysis, chemical structure, surface morphology, surface area, and porous structure of the synthesized aluminosilicates were characterized. The aluminosilicates were used as adsorbents in batch adsorption tests for removing phenol from water. The results showed that Langmuir isotherm had better fitting with experimental data than Freundlich isotherm. The results also showed that increasing in the silica concentration of the aluminosilicate improved the phenol adsorption due to ionic nature of Si–O bond. Ortho aminophenol and 2-naphtol adsorptions were also investigated and their maximum molar adsorption capacities were close to each other.

## Introduction

Phenolic compounds are carcinogenic and very dangerous for the environment and human health [1]. Phenol and its derivatives are introduced to the environment from wastewater of paint, pesticide, coal conversion, polymeric resin, and petroleum industries [1–3]. Because of the environmental hazards of phenolic contaminants, it is necessary to remove them from water. The most common techniques in removing phenol and organic pollutants from water include stripping, solvent extraction, ion exchange, adsorption, biodegradation, and chemical oxidation, of which adsorption is the most practical one because of its simplicity of operation, ease of regeneration, and low cost [1–3]. Due to importance of this issue, developing adsorbents with higher adsorption capacity and adjusting selectivity has been the subject of many research groups. Gupta et al. [1] used red mud, an aluminum industry waste, as an adsorbent for the removal of phenol and chlorophenols from wastewater. Anbia and Amirmahmoodi [2] prepared amino functional mesoporous silica SBA-15 and showed that $NH_2$-SBA-15 was a significant adsorbent for halophenols. Subramanyam and Das [3] studied two types of soils as adsorbent for removal of phenol from wastewater and found the equilibrium isotherms for the adsorption of phenol. Daifullah and Girgis [4] investigated the equilibrium removal of phenol and its derivatives by adsorption on activated carbon. Viraraghavan and Alfaro [5] found that the adsorption of phenol on peat and bentonite was described by Freundlich isotherm whereas the adsorption of phenol on fly ash was described by Langmuir isotherm. Nano zeolites composites were applied by Lu et al. [6] for removal of methyl tertiary butyl ether (MTBE) from water by adsorption.

Aluminosilicates are a group of adsorbents with high thermal stability and mechanical strength [6–8]. Aluminosilicates with high surface area and adjustable porosity have attracted many attentions [6–8]. In this study, nano structured aluminosilicates with different weight percentages of aluminum and silicon were prepared. They were synthesized using aluminum and silicon alkoxide and sol–gel methods. They were characterized by different techniques. These aluminosilicates were used as adsorbents and investigated for the removal of phenol, ortho aminophenol, and 2-naphtol from water. The adsorption isotherms of phenol, ortho aminophenol, and 2-naphtol were developed and discussed.

## Materials and methods

### *Reagents*

In the current study, aluminum isopropoxide, tetra ethyl ortho silane, nitric acid (63%) and ethanol (96%) from Merck Company were used for synthesizing the aluminosilicates. Deionized water was used as the reaction solvent. Phenol, ortho aminophenol, and 2-naphtol from Merck were used for preparing of the solutions to be used for adsorption tests.

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### *Synthesizing and characterization of the aluminosilicates*

a. **Alumina gel:** to prepare alumina gel, the method developed by Yoldas [9] was used. So, the deionized water was heated up to 85 °C, and aluminum isopropoxide was added and hydrolyzed. The solution was stirred at 85 °C for 1 h to vaporize the alcohol. Nitric acid was added so that the molar ratio of aluminum isopropoxide to water to nitric acid was 1:100:0.07. The mixture was constantly stirred at 85 °C for 24 h [9].
b. **Silica gel:** Nitric acid was added to the mixture of tetra ethyl ortho silane (TEOS) and ethanol. The TEOS/ethanol/nitric acid molar ratio was 1:100:0.07. The mixture was stirred at room temperature for 24 h [10,11].
c. **Aluminosilicate gel:** After adding nitric acid, the alumina sol of step ''a'' was mixed for 2 h and then silica sol of step ''b'' which had been mixed for 2 h was added. The mixture of alumina and silica sols was constantly stirred for 24 h [10,11]. By adding different amounts of silica sol to alumina sol, aluminosilicates with different weight percents of Al and Si were obtained.

The gel solutions of steps ''a'', ''b'', and ''c'' were dried in an oven at 100 °C for 24 h. The dried gels were calcined in a furnace at 600 °C for 2 h with the heating ramp of 3 °C/min.

The bulk elements of the synthesized aluminosilicates were measured by Philips PW 2404 XRF instrument. Fourier transform infrared (FT-IR) spectra of the samples, on KBr pellets, were measured with Bruker Vector 22 spectrometer. SEM images were taken by scanning electron microscope, Hitachi S-4160 model. The specific surface area and porosity of the samples were measured at 77 K by ASAP Micrometrics 2011. Before measuring nitrogen adsorption, the samples were degassed at 300 °C for 6 h. X-ray photoelectron spectra were obtained using a VG Microtech XR3E2 spectrometer equipped with an Al Kα (1486.6 eV) X-ray source. The base pressure in the analysis chamber was $10^{-9}$ Torr. UV-Vis spectrometer Varian Cary 50 model was used for measuring UV-Vis spectra of organic solute in water.

### *Adsorption tests*

10 mg of one of the synthesized aluminosilicates was added to a 25 ml of phenol solution of 350 mg/L concentration. The mixture was constantly stirred at room temperature (20 °C) for 24 h. After adsorption, the sample was centrifuged and the concentration of the supernatant was determined by UV-Vis spectrometer. The UV absorbance at 275 nm and Beer–Lambert law were used to measure the phenol concentration in the water solution. The phenol concentration was changed in the range of 50–350 mg/L and the adsorption tests were repeated. Each test was repeated three times. All the synthesized aluminosilicates were tested.

The above tests were also administered with the solutions of ortho aminophenol and 2-naphtol in the concentration range of 50–350 mg/L. The UV absorbance at 300 nm and 350 nm were used to measure the concentrations of the ortho aminophenol and 2-naphtol solutions, respectively.

## Results and discussion

### *Aluminosilicate characterization*

Adsorbent A is made up of only alumimum isopropoxide, so it is pure alumina and adsorbent E is made up of only tetra ethyl ortho silane, and is pure silica. Adsorbents B, C, and D are aluminosilicates or mixtures of alumina and silica which were analyzed by XRF and their weights and analyses were determined. Adsorbent B is 29.77% $SiO_2$, 70.23% $Al_2O_3$, adsorbent C is 50.43% $SiO_2$, 49.56% $Al_2O_3$, and adsorbent D is 67.69% $SiO_2$, 32.32% $Al_2O_3$.

Fig. 1 shows the infrared spectra of adsorbents A–E. All of the spectra have a broad absorption of O–H stretching vibration around 3550 $cm^{-1}$ [12]. The spectra of adsorbents B–E have a band at 1100 $cm^{-1}$ which corresponds to Si–O stretching vibration [13] and the intensities of the peaks raise with increasing $SiO_2$ concentration of the adsorbents. In adsorbent A, a broad band appears at 900 $cm^{-1}$ which reveals the formation of amorphous nano $Al_2O_3$ [12], whereas in the spectra of adsorbents B, C, and D; this band disappears because of its overlap with Si–O stretching vibration band at 1100 $cm^{-1}$.

Fig. 2 shows SEM images of adsorbents A–E with magnification of 150 × 1000. The SEM images show that the surface morphologies of these adsorbents are similar and the grain size is below 100 nm in all adsorbents.

Table 1 shows the BET surface area, average pore diameter, and pores volume. The BET surface area is increased with increase in the Si concentration from adsorbent A to D. Adsorbent E is pure silica and its BET surface area is less than adsorbents B, C, and D. The nitrogen adsorption/desorption isotherms of adsorbents from A to D, shown in Fig. 3, are IUPAC type IV. The hysteresis loops show that the adsorbents A–D have the same characteristics type of the hysteresis type H2 solids. The pores in these solid have different size of mouth and body like an ink bottle [14]. In adsorbent E, the nitrogen adsorption/desorption isotherm, as shown in Fig. 3, is IUPAC type I and hysteresis loop is type H4 with slit-shaped pores [14]. Fig. 4 shows that the pores have diameters less than 10 nm, meaning that all the adsorbents are mesopore. Adsorbent A is unimodal, and in the other adsorbents, the prevalence of the pores decreases as pore diameter increases.

XPS spectra for Al 2p and Si 2p of the adsorbent C are shown in Figs. 5 and 6. The peaks which are related to Al 2p XPS spectra are shown in Fig. 5. The peaks at 76.06 eV to Al 2p 3/2, 73.32 eV to Al 2p ½, 74.63 eV to AlOOH, and 77.53 eV to $Al(OH)_3$ are related [15,16]. Fig. 6 shows Si 2p XPS spectra. The peaks at 100.16 eV to Si 2p, 102.32 eV to $SiO_x$ ($x < 2$), and 103.5 eV to $SiO_2$ are related. XPS analysis also indicated 10.8% of Si is in the form of $SiO_2$, 62.8% of Si is in the form of $SiO_x$ ($x < 2$), and 26.4% of Si in the element form [16,17].

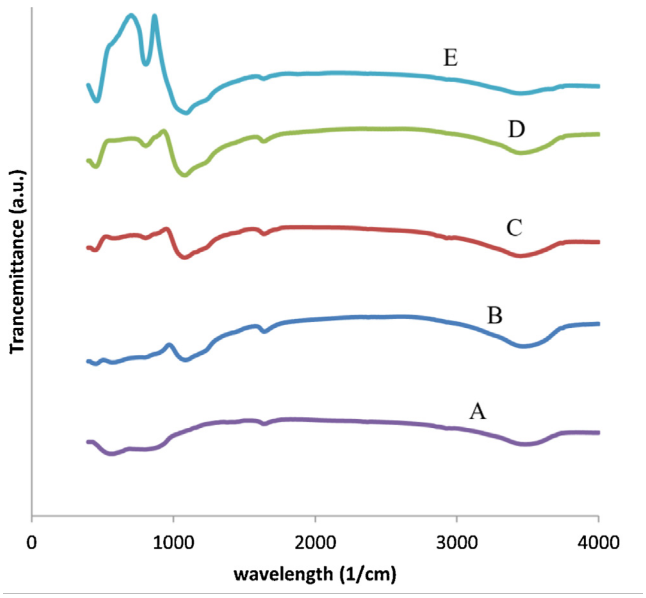

**Fig. 1.** FT-IR spectra of adsorbents A–E.