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Application of zeolite prepared from Egyptian kaolin for removal of heavy metals: I. Optimum conditions

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The optimum conditions for removal of heavy metals using zeolites A and X prepared from local kaolin zeolite were studied in order to apply it in industrial wastewater treatment. Metal removal was investigated using synthetic solutions at initial concentrations of 20 mg/L of individual metals (Cd, Cu, Pb, Zn and Ni) and mixture of the pre-mentioned metals with concentration of 20 mg/L for each at constant temperature and pH (25 ± 0.1 °C and 7.5 ± 0.2) respectively. The removal efficiency was determined at different contact time and different zeolite doses.

The optimum contact time for removal of Cd, Cu, Pb and Zn was 30 min for both zeolite types. On the other hand, optimum contact time for Ni removal was 60 min for both zeolite types. 0.8 g was the optimum dose for removal of all metals in case of zeolite X. The same trend was obtained in case of zeolite A except for Pb removal which has an optimum dose of 0.4 g.

Locally prepared zeolites A and X were highly efficient in heavy metal removal at optimum conditions and nearly equal due to presence of 8 faces including nanometer pours in the prepared zeolite enabling it for being effective in some molecular sieve separation of small molecules. The adsorption and desorption behaviours with respect to the studied metals are investigated in the running work.

1. Introduction

The optimization of water and wastewater purification processes requires the development of new operations based on low-cost raw materials with high pollutant-removal efficiency. Many toxic heavy metals are being discharged into the environment as industrial wastes, causing serious soil and water pollution [1]. Heavy metals such as zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni) and copper (Cu) are prior toxic pollutants in industrial wastewater, which become common groundwater contaminants and they tend to accumulate in organisms, causing numerous diseases and disorders [2]. The complexity of effluents makes the process of heavy metals removal more difficult due to presence of organic legends, phosphate, cyanide and humic matter that can be added to complexity of removal, as well as strict limitations that have been imposed to wastewater discharge everywhere in aquatic recipients [3].

Natural zeolites are safe, environmentally friendly, naturally occurring minerals that are aluminosilicates and have an open box-work crystal structure which is occupied by cations and water molecules. These ions and water molecules can move within the large cavities allowing ionic exchange and reversible rehydration. The structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion (Al) is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation [sodium (Na), potassium (K), or calcium (Ca)]. These cations are exchangeable with certain cations in solutions such as Pb, Cd, Zn, and Mn [4]. The fact that zeolite exchangeable ions are relatively innocuous (Na, Ca, and K ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. One of the earliest applications of a natural zeolite was in removal and purification of cesium (Cs) and strontium (Sr) radioisotopes [5]. So, zeolites can transfer a heavy metal contamination problem of many thousands of liters to a few kilos of easily handled solid. The toxic metals are firmly held in the crystal structure and do not leach, however for ultimate environmental protection the solid zeolite can be cement stabilized or vitrified [6].

Furthermore, natural zeolites are classified as low-cost adsorbents because of their local availability and low-cost extraction and preparation. Natural zeolites also gained a significant interest among scientist, mainly due to their valuable properties such as ion exchange ability and high surface areas. Zeolites offer a potential for a variety of industrial uses including molecular sieves, ion-exchangers, adsorbers, catalysts, detergent builders [7–9], the removal of cations from acid mine drainage and industrial wastewater [10]. Also, Leppert (1990) [11] reported that zeolites, have strong affinity for heavy metal ions.

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The objective of the present study is to investigate the performance and capacity of two zeolite types (A and X) in removal of heavy metals as either single metals or mixtures.

2. Material and methods

2.1. Preparation of zeolites for laboratory experiments

Zeolite was prepared using an Egyptian kaolin which analyzed *via* X-ray fluorescence. The chemical composition and physical properties of natural Egyptian kaolin are shown in Table (1).

Commercial sodium silicate solution ($Na_2Si_2O_5$) was used as source for silicone and commercial sodium hydroxide was used as alkaline solution with different concentration percent according to type of prepared zeolites.

Preparation of the two types of zeolite was adopted by Selim and Abd El-Maksoud, 2005 and 2006 [12,13]:

- Zeolite A was prepared according to Egyptian Patent.
- Zeolite X was prepared according to Egyptian Patent No. 23590-2006 Table (2).

Zeolite A and zeolite X which synthesized as mentioned above, were crushed, grounded and passed through different sieves until finally passed through 30 µm sieves (in order to determine the particle size of the used zeolites) and was dried in an oven at 100 ± 5 °C for 24 h.

2.2. Characterization of zeolites

All prepared zeolites were characterized with X-ray diffraction (XDR), using instrument Bruker D8 advance instrument with CuKα1 target with secondly monochromator 40 kV, 40 mA. Scanning electron microscope (SEM) of different samples and EDX analysis was performed using instrument "JXA-840 a Electron probe Micro Analyzer-Japan", Electron Spin Resonance was measured on (Brucker Elexsys. 500) operated at X-band frequency. The following parameters are generalized to all samples: Microwave frequency: 9.73 GHz, Receiver Gain: 20, Sweep width: 6000 center at 3480, Microwave power: 0.00202637. The infrared spectra were recorded in potassium bromide disks Shimadzu FT IR 8101 PC infrared spectrophotometers. Egyptian kaolin used in preparation of zeolite was analyzed on Axios, Sequential WD-XRF Spectrometer PANalytical 2005. Pore diameter was estimated by Gemini 2360 surface area analyzer.

2.3. Preparation of synthetic solutions of metals

Inorganic chemicals were supplied by Merck as analytical-grade reagents. The metal ions studied were Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II). A synthetic stock solution of Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II) using $CdCl_2.5/2H_2O$, $CuSO_4.5H_2O$, $NiCl_2.6H_2O$, $Pb(CH_3COO)_2.3H_2O$ and $ZnSO_4.7H_2O$, respectively, in deionized water.

Table 1
Chemical composition and physical composition of natural Egyptian kaolin (wt.%).

Chemical composition (%)		Physical composition	
SiO_2	52.7	pH	7.5
Al_2O_3	31.4	Appearance porosity (%)	41
TiO_2	2.2	Appearance density (g//cm^3)	2.20
Fe_2O_3	1.1	Weight of per unit volume (g/cm^3)	1.30
MnO	0.01	Water absorption (original) (%)	30.3
MgO	0.21	Water absorption (grinding) (%)	102.6
CaO	0.52	Original bleaching (g sample/g tonsil)	1.94
Na_2O	0.1	Active bleaching (g sample/g tonsil)	1.90
K_2O	0.04	Ignition loss	0.14
P_2O_5	0.08		
SO_3	0.14		

Table 2
The preparation percent for zeolite A and zeolite X.

Zeolite	Reaction composition (moles/Al_2O_3)		
	Na_2O	SiO_2	H_2O
Zeolite A	3.5	2.2	140
Zeolite X	7.8	8	200

2.4. Analytical methods

2.4.1. Determination of trace-metal concentration

The concentrations of heavy metals in all samples were determined according to APHA (2005) [14] using Atomic Absorption Spectrometer Varian SpectrAA (220) with graphite furnace accessory and equipped with deuterium arc background corrector. Precision of the metal measurement was determined by analyzing (in triplicate) the metal concentration of all samples and for each series of measurements an absorption calibration curve was constructed composed of a blank and three or more standards.

2.5. Quality control

For each series of measurements absorption calibration curve was constructed composed of a blank and three or more standards from Merck Germany. Accuracy and precision of the metals measurement were confirmed using external reference standards from Merck, and standard reference material 1643e for trace elements in water and quality control sample from National Institute Standards and Technology (NIST), were used to confirm the instrument metal concentration reading.

Element	Unit	Instrument detection limit
Cd	mg/L	0.002
Cu	mg/L	0.01
Ni	mg/L	0.02
Pb	mg/L	0.05
Zn	mg/L	0.005

2.6. Batch adsorption studies

2.6.1. Determination of optimum dose and contact time

The laboratory-scale experimental studies were conducted using synthetic solutions prepared using deionized water with constant metal concentration for each of Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II) separately and their mixture (mixture of all the pre-mentioned metals in 20 mg/L for each). The uptake of heavy metals on the two types of zeolites was carried out using the batch method.

Batch adsorption experiments were conducted using different dose of zeolites that ranged from 0.1 to 1 g with 100 ml of solutions containing heavy metal ions of desired concentrations (20 mg/l) for each metals at constant temperature (25 ± 0.1 °C) and constant pH (7.5 ± 0.2) in 150-ml glass bottles. The bottles were shaken in a rotary shaker at200 rpm form 5 min. to 24 h and solutions containing heavy metals were filtered through Whatman filter paper (No. 42).

2.7. Optimum contact time

Batch adsorption experiment was conducted for removal of studied heavy metal at temperature (25 ± 0.1 °C) and pH (7.5 ± 0.1) with different time intervals in order to determine the optimum contact time. zeolite A and zeolite X were applied to remove Cd (II), Cu (II), Pb (II), Ni (II) and Zn (II) from synthetic water samples of 20 mg/L