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Removal of cyanide using surface-modified Linde Type-A zeolite nanoparticles as an efficient and eco-friendly material

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ABSTRACT

Linde Type-A (LTA) zeolite nanoparticles were synthesized, modified with hexadecyltrimethylammonium bromide, and then used for removal of cyanide from synthetic solution. The synthesized adsorbent was characterized by means of XRD, SEM, FTIR, and BET techniques. Results well revealed that the cyanide adsorption rate increased with increase in solution temperature, and the pseudo second-order model best describe the cyanide adsorption kinetics. The changes in enthalpy (ΔH°) and entropy (ΔS°) were −434 kJ/mol and 5.32 kJ/mol K, respectively, which substantiates the spontaneous and exothermic behaviour of the cyanide uptake by modified LTA zeolite nanoparticles. The experimental isotherm results were best fitted onto the Langmuir monolayer model with a maximum adsorption capacity of 24.09 mg/g; this value is higher than the previously reported values for other adsorbents, and thereby demonstrates that modified LTA zeolite is an efficient adsorbent material for cyanide removal.

1. Introduction

The increasing water resources contamination by industrial wastewater containing toxic materials possesses a critical environmental issue [1]. Cyanide is a hazardous pollutant of special interest that attracts considerable attention wing to its fatal effects on human health and environment [2]. Cyanide is extremely toxic to human health that is used in a several industries and detected in low amounts from car exhausts. Chronic exposure of humans to cyanide primarily has detrimental effects on the central nervous system [3], apart from affecting the cardiovascular and respiratory systems, enlarging thyroid glands, and causing irritation to the eyes and skin [4]. No data are available on the carcinogenic effects of cyanide in humans as a consequence of its inhalation [3], although many researchers have reported adverse effects of cyanide. Cyanide is in two dangerous forms namely HCN and CN^- in water [5]. Cyanide-contaminated wastewater are produced from several industries, for example, industrial effluents from gold extraction, iron and steel, oil extraction and refining, as well as metal plating industries contain cyanide species above the maximum contaminant level allowed [6,7]. Therefore, these effluents must be treated before discharging them into any aquatic environment. For that reason and for environmental protection goals, the Environmental Protection Agency (EPA) set strong standards on the acceptable cyanide levels in industrial wastewater effluent which is suggested to be below 0.2 mg/L prior to discharge into the environment [8]. In the USA, according to EPA standards, the allowed cyanide level in drinking water and aquatic environment are 200 and 50 ppb, respectively, and, generally, the local environmental discharge limit is 0.2 ppm [9,10]. Numerous procedures have been proposed for cyanide treatment in wastewater including electro-winning [11], hydrolysis–distillation [9], flotation [12], iron-cyanide precipitation [13], resin [14], acidification–volatilisation–re-neutralisation [15], reverse osmosis [16], degradation by hydrogen peroxide [17], oxidation by Caro's acid [18], and biosorption [19]. In the design of appropriate treatment method, the concentration of waste and the cost of treatment method must be taken into account [20]. Adsorption is a low-cost, simple, and widely used method for treating various toxic materials [5]. Nowadays, nanoadsorbent defined by including nano cavity, have received great notice for the removal of pollutant due to their high surface area which is followed higher adsorption capacities. Recently, adsorption using zeolitic materials in nano size has attracted much attention in environmental applications [21,22]. Moreover, extraordinary adsorption, catalysis, and ion-exchange properties of zeolite have found numerous industrial and research applications in the bulk powder form [23]. Linde Type-A (LTA)

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zeolite materials are crystalline compounds with an extremely ordered and open microporous frame consisting of a three-dimensional network of SiO_4 and AlO_4 tetrahedral [24]. LTA zeolite is a well-known type of zeolitic material in terms of large-scale commercial production and application [5]. LTA zeolite has been described as sodalite cages linked via four-membered rings. The bounding layout of the sodalite cages leads in the formation of a large central hole known as a super cage. After that, the LTA zeolite is formed by bonding of this central cavity with six similar cavities via an eight-ring window of an opening diameter of 4.2 Å. The synthetic LTA zeolite has a Si/Al ratio of 1, however, higher ratios (up to 1.7) may be observed when tetramethylammonium is used as starting materials in the synthesis of LTA zeolite [5]. To enhance the adsorption capacity, LTA zeolite nanoparticles may be subjected to a sequence of processes in order to modify its surface, which can be done using a cationic surfactant. By modification of zeolites with cationic surfactant, a positive functional group was created on the external surfaces and the charge density was changed to positive side. Therefore, such zeolite will be appropriate for adsorption of negatively charged materials such as cyanide [25]. Generally, hexadecyltrimethylammonium bromide (HDTMAB) is applied for this purpose, which is a quaternary amine with a long-chain cationic surfactant [26]. Recently, interest in the adsorption of anions and nonpolar molecules on surface-modified zeolites has increased. For example, the adsorption of aromatic hydrocarbons, methyltert-butylether (MTBE), BTEX, and other petroleum monoaromatics from contaminated aqueous solutions on granulated natural zeolite nanoparticles modified with surfactant has been studied [27–29,23]. The aim of present study was the synthesis of LTA zeolite nanoparticles, modify of it by HDTMAB and then evaluate of their ability for removal of cyanide from aqueous samples.

2. Materials and methods

2.1. Chemicals

Analytical grade chemicals were used for experimental studies. NaCN; hexadecyltrimethylammonium bromide (HDTMAB); Silicon dioxide (SiO_2); Aluminum oxide (Al_2O_3); Ethanol (EtOH), and Propanol (PrOH) were purchased from Merck Co. (Germany). The initial cyanide solution (1000 mg/L) was prepared by adding a 1.88 g of powdered NaCN in deionized water and then diluted to the different practical concentrations (25–75 mg/L). Cyanide concentrations were measured by Argentimetric titrations, according to standard methods for the examination of water and wastewater (method 4500-CN-D) [30]. The pH of solution was adjusted by 1 M H_2SO_4 and NaOH and measured by a pH-meter (Jenway, Model 3510).

2.2. Adsorbent characterization

The scanning electron microscope (SEM) using Philips-XL30 instrument (Netherlands) equipped with energy-dispersive X-ray microanalysis (EDX) was used for adsorbent surface morphology studies and elemental analysis. The specific surface area of the adsorbent was determined using a nitrogen adsorption technique based on the Brunauer–Emmet–Teller (BET) isotherm model (Micromeretics/Gemini-2372). The nature of involved functional groups in cyanide adsorption on the surface of the adsorbent was determined by Fourier-transformed infrared spectroscopy (FTIR) at a wavelength range of 400–4000 cm^{-1} (Bruker-VERTEX 70, Germany). The elemental analysis of the adsorbent samples was conducted by using an EDX spectrometer attached to the SEM. Moreover, X-ray diffraction (XRD) instrument using the PHILIPS Xpert Pro with CuKα radiation (1.54056Åwavelength) generated at 40 kV/40 mA with a fixed divergence step width of 0.02° (2θ) at a scanning rate of 8°/min was used for identifying the crystalline pattern of the used adsorbent (Philips Electronics Co., Netherlands).

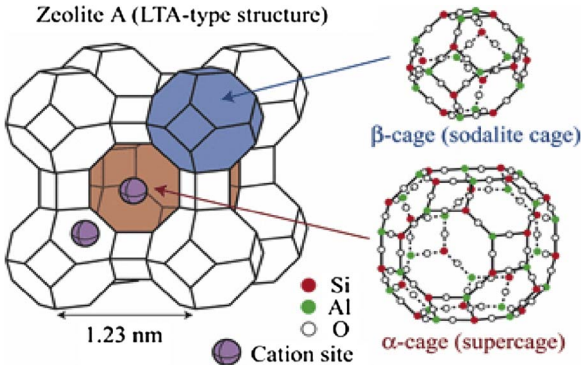

Fig. 1. Schematic representation of LTA zeolite structure [31].

2.3. Preparation of the adsorbent

In this study, an LTA zeolite nanoparticle modified by HDTMAB was applied for uptake of cyanide from a synthetic solution. In the beginning, LTA zeolite was synthesized in the laboratory from a homogenized mixture solution of the following molar composition: $0.8NaOH/5.0HDTMAB/3.4SiO_2/1.0Al_2O_3/370H_2O/19.6EtOH/6.0$iso-PrOH. The molecular structure of the LTA zeolite is shown in Fig. 1 [31]. LTA zeolite was crystallised in a sealed polypropylene bottle and then stirred vigorously at 98 °C for 3 h. The LTA zeolite nanoparticles were recovered from the mother liquor by centrifugation using a centrifuge (Sigma-301, 159 Germany) at 12000 rpm for 60 min. Next, to remove any unreacted materials, the LTA zeolite nanoparticles powder was dispersed in deionized water by sonication and then centrifugation. This procedure was repeated until the pH of the supernatant dropped below 9. The LTA zeolite nanoparticles powder was dried at 65 °C over night and then calcined at 500 °C for 4 h in an electrical furnace. The heating and cooling order was set at 1 °C/min to remove the HDTMAB molecules.

2.4. Surface modification of adsorbent

The surface modification of LTA zeolite nanoparticles was performed using HDTMAB. Briefly, 10 g of powdered raw synthesis LTA zeolite was introduced to 1000 mL HDTMAB solution and the solution was placed on a shaker (Hanna-Hi 157 190 M, Singapore)for 24 h at 60 °C. After 24 h, the modified zeolite was separated by centrifuging of solution at 12000 rpm for 5 min. The modified adsorbent was then washed twice with 100 mL of deionized water, stirred at 150 rpm for 15 min, and then centrifuged at 12000 rpm for 5 min. The pH of the final solutions was registered and found to be7.0 ± 0.2. Next, the centrifuged material of modified LTA zeolite was dried at 110 °C for 24 h and kept in a glass container for subsequent use in the adsorption tests.

2.5. Experiments

Batch adsorption experiments were conducted in 250 mL conical flasks. All experiments were conducted at the room temperature; expect those meant for the effects of temperature study. Various experimental parameters such as pH (3–11), temperature (20–60 °C), adsorbent mass (0.2–1 g/L), initial cyanide concentration (25, 50, and 75 mg/L) and contact time (0–120 min) were investigated. At first, kinetic of adsorption and effect of initial cyanide concentration on the removal efficiency were performed at pH 7. Adsorbent of 0.5 g/L was introduced into three conical flasks containing the cyanide solution at a concentration of 25, 50, and 75 mg/L. These flasks were shaken at 200 rpm. At a predetermined time interval, the samples were collected, filtered through a filter paper (0.45 mm; Whatman, Germany), and then centrifuged. The residual cyanide concentration was then determined