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Research paper

CTAB modified large surface area nanoporous geopolymer with high adsorption capacity for copper ion removal

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ABSTRACT

Nanoporous geopolymer was synthesized with and without using Cetyl trimethylammonium bromide (CTAB) by condensing the mixture of metakaolin and alkali solution at a fixed ratio at room temperature. The surface area of CTAB-geopolymer was found to be more (216 m^2/g) as compared to without CTAB added geopolymer (137 m^2/g). The experimental results verified that the geopolymer could adsorb copper ions completely at lower concentrations and partially at higher concentrations. Pseudo second order model fits well at all the concentration from 55 to 1700 ppm as the values of the correlation coefficient lies between 0.96 and 0.99. Intraparticle diffusion model at the concentration 55 ppm explains that there is only boundary layer diffusion (instantaneous) and after this step, all the Cu ions are exchanged by the nanoporous geopolymer. At 120 ppm, intraparticle diffusion model shows multilinearity. Different adsorption models - Langmuir, Freundlich and Tempkin were also tested to evaluate the most appropriate model and it was found that adsorption follows Langmuir model. The adsorption capacity and pseudo second order rate constant is estimated to be 1.65 meq/g which is significantly higher than the fly ash based nonporous geopolymer.

1. Introduction

Geopolymers, also called polysialates, are a class of amorphous aluminosilicate materials formed near ambient temperature. Chemically, geopolymers consist of cross-lined units of AlO_4^- and SiO_4 tetrahedra, where charge-balancing cations are provided by alkali metal cations such as Li^+, Na^+, K^+, and Cs^+. It has already been demonstrated in the previous studies that geopolymers could be prepared from metakaolin or wastes, such as slag, fly ash and tailing (Duxson et al., 2007; Goretta et al., 2007). This makes geopolymer an important material as these precursors are highly cost effective and can be easily obtained in bulk. Geopolymers have applications such as fire- and heat-resistant coatings and adhesives, medicinal applications, high-temperature ceramics, new binders for fire-resistant fiber composites, toxic and radioactive waste encapsulation and as cementing components to make concrete (Davidovits, 2015). In addition to these applications, geopolymers are being used as a substrate in adsorption process due of their low cost, excellent mechanical and physical properties, low energy consumption and green synthesis process. In regards to adsorption, they have been mainly explored for removing heavy metals from wastewater (Cheng et al., 2012; Medpelli et al., 2015). The removal of heavy metals from the environment is necessary because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentration (Bansal et al., 2009). Although removal of heavy metals from waste water can be done by using a large number of techniques, such as, ion exchange (Kang et al., 2004), reverse osmosis (Mohsen-Nia et al., 2007), chemical coagulation (Chang and Wang, 2007), chemical precipitations (Ku and Jung, 2001) and solvent extraction (Černá, 1995), adsorption however remains a very attractive method (Bhattacharyya and Gupta, 2008; Jusoh et al., 2007; Li et al., 2010) due to its simplistic methodology, effectiveness, and low cost for heavy metal wastewater treatment. Adsorption also offers flexibility in design and operation and in many cases produces high-quality treated effluent. Another advantage of adsorption process is that it is sometimes reversible, and hence adsorbents can be regenerated by suitable desorption process. Methods other than adsorption may possibly be very effective but have high capital and operation costs and the problem of residual disposal.

Among the heavy metals, copper metal is very hazardous to human health and the environment. Copper is generated in metal cleaning and plating baths, paper, paperboard mills, wood-pulp production, tire manufacture, and fertilizer industries and is accumulating in their waste streams (Wang et al., 2007). Adsorption of Cu^{2+} has short and long term effects on human health. Many effective methods are used for

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copper removal from wastewater including chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption. Cheng et al. (2012) recently demonstrated the adsorption capacity of metakaolin based geopolymer toward Pb(II), Cu (II), Cr(III) and Cd(II). Kara et al. (2017) reported also Metakaolin based geopolymer as an effective adsorbent for adsorption of zinc(II) and nickel(II) ions from aqueous solutions. The removal of copper ions has been achieved by fly ash based geopolymer (Al-Harahsheh et al., 2015; Wang et al., 2007). The effects of zeolitic tuffs implemented as a filler on the mechanical performance and adsorption capacity of geopolymer products has been investigated by Yousef et al. (2009) for methylene blue and Cu^{2+}. Porous geopolymers have been used to adsorb copper ions with good adsorption capacity (Andrejkovičová et al., 2016; Cheng et al., 2012; Ge et al., 2015; López et al., 2014; Tang et al., 2015). Similarly, there are many studies devoted to the use of geopolymer for copper ion removal (Duan et al., 2016; El-Eswed et al., 2012; Ge et al., 2017; Taskin et al., 2016; Yunsheng et al., 2007; Zhang et al., 2008). In addition to copper, geopolymers have also been used to adsorb of Ca^{2+} and Mg^{2+} for softening the water (Naghsh and Shams, 2017).

In spite of many reports in the literature there are very few reports where the use of high surface area nanoporous geopolymer has been used for removal of metals (Medpelli et al., 2015). Hence, in the present work we have demonstrated the synthesis of metakaolin-based high surface area nanoporous geopolymers using CTAB as the surfactant. We further demonstrate its efficiency for the adsorption of copper ions. Nanoporous geopolymer will be important as its high surface area will lead to high adsorption capacity toward metal ions. We have focused on the removal of copper ions as they are one the major pollutants present in the surface and ground water coming from industries.

2. Materials and methods

2.1. Synthesis

14 g of KOH is dissolved in 32 mL of distilled water in a polypropylene beaker. To the aqueous solution of KOH, 15.43 g of fumed silica is slowly added and then stirred with mechanical stirrer for 30 min at 800 rpm. To the obtained clear solution, 10 g of metakaolin is slowly added and dissolved properly. Metakaolin is prepared by calcining kaolinite at 750 °C for 10 h to cause dehydration, and thus increasing reaction activity. Resin thus formed is cured in oven at 60° C for 24 h. A light brown colored (geopolymer) cured product is broken into small pieces and washed with cold distilled water to remove excess alkali. The sample is then crushed and sieved to control the particle size range of 14–16 mesh.

In order to increase the porosity of the geopolymer a modification was made in the synthesis methodology. Cetyl trimethylammonium bromide (CTAB) was added before the addition of metakaolin during synthesis. The remaining procedure remained same. Both the geopolymers (without using CTAB and with using CTAB) were characterized by X-ray diffraction (XRD) by using BRUKER D8 DISCOVER diffractometer in the range of 10–80° for crystallinity, Fourier transform infrared (FTIR) for surface functional groups was done using THERMOSCIENTIFIC (IS50) and scanning electron microscopy (SEM) for microstructure evaluation was done by using JOEL (JSM-7600F). The Brunauer–Emmer–Teller (BET) surface area and pore properties were measured by a N_2 adsorption–desorption isotherm at liquid nitrogen temperature by using (Micromeritics 3-Flex, USA), and utilizing N_2 as adsorbate after drying at 200 °C. Pore size distributions were obtained using the Barrett–Joyner–Halenda (BJH) method assuming a cylindrical pore model (Barrett et al., 1951).

2.2. Adsorption experiment

Adsorption experiments were carried out using 200 mg of nanoporous geopolymer and using varied concentrations of $Cu(NO_3)\cdot 3H_2O$ as a source of Cu^{2+}. Nanoporous geopolymer was in the form of 30/40 grain size (500 μm) so as to make its separation easy from the solution. 200 mg of the nanoporous geopolymer was added to 50 mL of Cu^{2+} solution of 55, 120, 160, 650, 1500 and 1700 ppm. Solutions were kept on stirring to facilitate the adsorption and dispersion of the nanoporous geopolymer. During this process, samples (1 mL) were collected from the reaction beaker at different time intervals, and the concentration of the Cu^{2+} solution was determined by UV–vis absorption spectroscopy (Perkin Elmer). The concentrations of Cu^{2+} solutions were calibrated using the Beer-Lambert law at λ_{max} of the blue colored tetraamminecopper complex made by the addition of 40% NH_4OH solution to the solutions of $Cu(NO_3)_2.3H_2O$. Change in the Cu^{2+} concentration with respect to time was plotted and using this measurement, kinetic models namely, pseudo second order and intraparticle diffusion models were tested. Further, adsorption models such as Langmuir, Freundlich and Tempkin were also tested to evaluate the most appropriate model.

3. Results and discussion

3.1. Characteristics of geopolymer

X-ray diffraction patterns of kaolinite, metakaolin (obtained by calcining kaolinite at 750 °C for 10 h), geopolymer synthesized without using CTAB and geopolymer using CTAB is shown in Fig. 1. Kaolin exists in three main crystalline phases - kaolinite, illite, and quartz. The three major peaks at 12, 25 and 27° in Fig. 1(a), matched exactly with the kaolinite phase, whereas, the small peaks at around 20° and between 30 and 40° were mixture of all the three phases of kaolin (Konan et al., 2009). The disappearance of the characteristic diffraction peaks of kaolinite in Fig. 1(b) suggests its transformation into metakaolin by heating at 750°C for 10 h. The XRD patterns of geopolymer without using CTAB and with CTAB (Fig. 1(c) and (d)) were found to be similar. A characteristic hump like feature between 20 and 30° confirms the formation of geopolymer.

Scanning electron microscopy was also used to analyze the morphology of all the samples (Figs. 2–5). The SEM images of kaolinite (Fig. 2(a) to (d)) showed chip like structure and no porosity was found in this compound. The SEM images of metakaolin (Fig. 3(a) to (d)) also showed similar morphology as kaolinite, however, the size appear smaller. Here also, the structure is largely nonporous although the particles are more connected in comparison to kaolinite. SEM images of

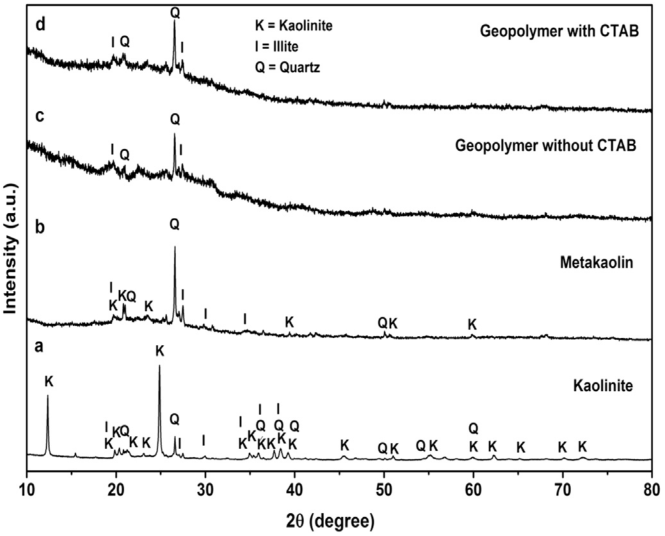

Fig. 1. X-ray diffraction patterns of (a) kaolinite, (b) metakaolin when kaolinite calcined at 750 °C for 10 h, (c) geopolymer without using CTAB, (d) geopolymer using CTAB.