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Efficient removal of hazardous lead, cadmium, and arsenic from aqueous environment by iron oxide modified clay-activated carbon composite beads

Radheshyam R. Pawar[a],[*], Lalhmunsiama[a], Munui Kim[a], Jae-Gyu Kim[a], Seong-Min Hong[b], Sandesh Y. Sawant[c], Seung Mok Lee[a],[*]

[a] Department of Environmental Engineering, Catholic Kwandong University, Gangneung 210-701, Republic of Korea
[b] Aqua Tech Co., Ltd., 525 Beon-gil, Yeoungtong-gu, Suwon 16706, Republic of Korea
[c] School of Chemical Engineering, Yeungnam University, Gyeongsan-si, Gyeongbuk 712-749, South Korea

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ABSTRACT

The present communication addresses the removal of toxic lead, cadmium, and arsenic using iron oxide modified clay-activated carbon composite beads from aqueous solutions. The SEM-EDX analysis was conducted to study the heterogeneity of the surface and the elemental composition of the composite beads. The specific surface area of the composite beads was found to be 433 m^2/g. Furthermore, the XRD pattern indicates the intercalation of iron particles between the layers of bentonite clay. The FT-IR analysis suggests that the hydroxyl, carboxyl, and Fe-O were the major functional groups responsible for the removal of lead, cadmium, and arsenic. The Langmuir monolayer sorption capacity of Pb(II), Cd(II) and As(V) were observed to be 74.2, 41.3 and 5.0 mg/g respectively. Kinetic studies indicate that intra-particle diffusion plays a significant role in the removal of these three toxic pollutants. In addition, the composite beads were applied for the adsorption of a ternary mixture of subjected pollutants at low concentrations and found efficient to remove these pollutants up to an acceptable permissible limit of drinking water. The significances of this study propose the potential of composite beads for purifying the water containing toxic pollutants, viz., lead, cadmium, and arsenic.

1. Introduction

The metal and metalloid toxic pollutants are widely dispersed in a human environment due to the rapid growth of industrialization and urbanization (Núñez et al., 2017; Zubair et al., 2017). The presence of hazardous toxic metal and metalloid ions in the aquatic environment is a major global concern because of its serious consequences for human's health (Li et al., 2018; Sawant et al., 2017; Sigdel et al., 2016). It is noteworthy to revealed that some of the metal ions such as iron, zinc, copper, cobalt, chromium, manganese and nickel are essential trace elements as they are required for biological metabolism in trace amounts; however, a high dose may cause toxic effects to living organisms (Asgari Lajayer et al., 2017; Ding et al., 2016). The toxic metal ions such as lead, cadmium, mercury and metalloids arsenite/ arsenate etc. are harmful to biological functions and they are the priority pollutants that are of serious concern for human health because of their high toxicity even at extremely low-level concentrations (Alipanahpour Dil et al., 2017; Asgari Lajayer et al., 2017; Ding et al., 2016; Rojas, 2014). Moreover, these types of several metal and metalloids are classified as human carcinogens according to the U.S. Environmental

Protection Agency and the International Agency for Research on Cancer (IARC) (Tchounwou et al., 2012). According to the Institute for health metrics and evaluation, more than half million deaths per year are caused by the lead exposure which has prompted research into the removal lead from water (Sawant et al., 2017). Cadmium is classified as a category 1 human carcinogen by IARC due to its potent characteristics with lung cancer, and also the occupational exposure to cadmium is associated with prostate, pancreas, and kidney cancers (Bediako et al., 2016; Fosso-Kankeu et al., 2017; Huff et al., 2007; Waisberg et al., 2003; Yap et al., 2017). Furthermore, the inorganic arsenic compounds are classified as Group 1 carcinogen by IARC (IARC Monographs, 2012) (Tokar et al., 2010). The ingestion of arsenic is found to be associated with skin, bladder, lung, kidney and liver cancers and this evidence comes from epidemiological studies of arsenic ore smelters, pesticide workers, and people exposed to arsenic-containing drinking water (Rossman, 2003).

Consequently, numerous studies are going on to develop suitable adsorbent for the removal of hazardous pollutants from the contaminated environment (Lee and Tiwari, 2012; Pawar et al., 2009; Sethia et al., 2014). Among the miscellaneous approaches, such as

adsorption, precipitation coagulation, electrodialysis, and membrane separation (Ingole et al., 2017). Generally, adsorption is one of the most common methods employed for treatment of toxic ions contaminated water due to its low cost, simplicity and high efficiency (Lee et al., 2017; Pawar et al., 2016a; Sawant et al., 2018b). In the past decades, composite material received a greater interest in environmental remediation especially in wastewater treatment technology due to its treatment efficiencies and multifunctional behavior (Reddy and Lee, 2013). The nanocrystalline cellulose-bentonite nanocomposite was used for the removal of Pb(II) and Hg(II) from aqueous solution in single and binary systems and this study observed that functional group plays a major role in the adsorption mechanisms (Putro et al., 2017). In another study, the removal of toxic heavy metal cations such as Cd(II), Hg(II), Pb(II), Co(II) and Zn(II) was performed using cysteine-montmorillonite composites and the adsorption capacity of the hybrid inorganic-organic materials was found to be higher than a pure montmorillonite (El Adraa et al., 2017). Moreover, graphene oxide and its composites are widely employed as an advanced adsorbent for the removal of toxic heavy metal ions from aqueous media and the possible adsorption mechanisms include electrostatic attraction, ion exchange and surface complexation (Peng et al., 2017). Several researchers report the preparation of composite beads and its application in wastewater remediation (Unuabonah and Taubert, 2014). The cross-linked activated organo-bentonite and sodium alginate composite beads were found to be low-cost adsorbent for the removal of cationic and anionic dyes (Belhouchat et al., 2017). The composite bead was prepared by immobilizing iron oxide modified sericite clay into Na-alginate using Fe (III) ions cross-linking agent and then successfully employed for As(V) and Pb(II) adsorption in water (Lalhmunsiama et al., 2017b). Moreover, chitosan/Poly(vinyl alcohol)/ZnO beads (Xu et al., 2017), Poly(vinyl alcohol) (PVA)/gelatin hydrogel beads (Hui et al., 2015), magnetic biosorbent hydrogel beads (Sahraei et al., 2017), Magnetite graphene oxide encapsulated in alginate beads (Vu et al., 2017), Zirconium phosphonate doped PVA/Chitosan hybrid gel beads (Jing et al., 2015), hectorite clay-alginate composite beads (Pawar et al., 2018) and many more polymer encapsulated adsorbents were successfully reported for the removal of various toxic pollutants from aqueous solutions. Therefore, these studies indicate that encapsulation of powder adsorbent materials into encapsulated beads possibly increased the feasibility of powder material in adsorption system for water purification.

The adsorption efficiency of heavy metals from aqueous solutions is greatly influenced by the speciation of metals in water. For instance, cadmium and lead mainly exist as the cationic Cd(II) and Pb(II) at lower pH and forms a precipitate at higher pH, whereas arsenic (arsenite or arsenate) mostly exist as anionic species or neutral species within a wide range of pH (3 to 10). It is interesting to develop the sustainable adsorbent which is capable to remove various toxic i.e., cationic and anionic toxic pollutants from the contaminated water (Santhosh et al., 2017). Therefore, the present study aims to develop a suitable adsorbent material by encapsulating the iron oxide modified bentonite clay and activated carbon into beads by biopolymer sodium alginate and then applied in the removal of cationic (lead and cadmium) as well as anionic (arsenate) toxic pollutants from the aqueous environment.

2. Materials and methods

2.1. Materials

The natural Bentonite sample with mineralogical chemical composition SiO_2: 56, Al_2O_3: 22, Fe_2O_3: 12.88, Na_2O: 2.22, MgO: 2.12, CaO: 0.88, TiO_2: 2.44% and Na-Alginate were procured from Dae-Jung Chemicals and Metals Co. Ltd. South Korea. The commercial activated carbon used was prepared from the coconut shell. The chemicals viz., nitric acid, sodium hydroxide, iron nitrate were obtained from Duksan Pure Chemicals Co. Ltd., Korea. And standard solutions for AAS were purchased from Fisher Scientific, from Sigma Aldrich, Germany. Lead

(II) nitrate, cadmium (II) nitrate (Junsei Chemical Co. Ltd., Japan), disodium hydrogen arsenate heptahydrate (Wako Pure Chemicals Industries ltd., Japan) the respective metal salts were used for the preparation of 1000 mg/L Pb(II), Cd(II) and As(V) stock solutions. The water used in all the experiments was purified by Millipore water purification system (Milli-Q+). The 50 μg/L of Cd(II), Pb(II) and As(V) synthetic solutions were prepared by successive dilution from 10 mg/L solution. The concentration of these toxic ions will remain almost unchanged for a long period of time if stored in a closed polyethylene container.

2.2. Preparation of composite beads

Initially, 0.1 mol/L $Fe(NO_3)_3.9H_2O$ solution was prepared in 1000 mLbeaker and 6 mol/L NaOH was slowly added with continuous stirring until the pH was adjusted at 7.5 to formed a precipitated Fe $(OH)_2$. 40 g of bentonite powder was added into this solution and continuously stirred for 3 h. And then, 40 g of activated carbon was added into the above mixture and again vigorously stirred for 3 h. The slurry was allowed to settle at the bottom and separated from the excess water. It was dried in a hot air oven at 120 °C. The iron oxide modified bentonite-activated carbon was utilized in the preparation of composite beads.

The composite bead was prepared as follows: 8 g of Na-alginate was dispersed in 650 mL of distilled water under continuous stirring. After homogeneity, 40 g of iron oxide modified bentonite-activated carbon powder was added to the alginate suspension and thoroughly mixed using mechanical stirrer. After homogenously blended, the mixture was slowly drops using a separatory funnel into an aqueous coagulation bath containing 2000 mL solution of 2% $CaCl_2$ which was continuously stirred using magnetic stirrer. The wet beads obtained have uniform spherical shape with the diameter range of 3.5 to 4 mm. The beads were separated and washed with pure water for several times and completely dried in a hot air oven at 80 °C and kept for further use. The dry beads were an easy to handle and suitable for batch sorption study. The photograph of the dried beads is shown in Fig. 1, a diameter of the dried beads was measured and observed in the range of 2–3 mm. The bulk density for the dried beads was calculated based on their mass (m) to volume (v) ratios as 0.84 g/cm³.

2.3. Characterization of materials

The surface morphology of the composite beads and other pristine material was captured by scanning electron microscope (SEM) and the

Fig. 1. Photograph of iron oxide modified clay-activated carbon composite dry beads.