



Research paper

Inorganically modified clay minerals: Preparation, characterization, and arsenic adsorption in contaminated water and soil

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ABSTRACT

The use of modified clay minerals for adsorbing arsenic (As) in contaminated soils is an underexplored area of research. The adsorption behavior of As onto inorganically modified smectite and kaolinite both in aqueous and soil media was studied. X-ray diffraction, infra-red spectroscopy, scanning and transmission electron microscopy studies confirmed successful modification of smectite through Fe-exchange and Ti-pillaring, and kaolinite through phosphate binding. The modified smectites were more efficient than phosphate-bound kaolinite in adsorbing As both in water and soil systems. Kinetic study revealed that the clay products reached adsorption equilibrium within 3 h, and the data well fitted to the power function and simple Elovich equation ($R^2 > 0.90$). The Freundlich isotherm model best described the As adsorption data ($R^2 > 0.86$) of the modified clay products in both the systems. The Ti-pillared smectite exhibited the highest As adsorption capacity ($156.54 \mu\text{g g}^{-1}$) in the aqueous medium, while the Fe-exchanged smectite was the best material in the soil system ($115.63 \mu\text{g g}^{-1}$). The partition coefficient (K_d) and adsorption efficiency (%) data also maintained the similar trend. Precipitation of As and binuclear complex formation also took place in the soil system which made the metalloid non-labile as the time passed. The inorganically modified clay products reported here hold a great potential to adsorb As in contaminated groundwater, drinking water as well as soil.

1. Introduction

Arsenic (As) has become a major pollutant in soil and drinking water in many parts of the world. Despite being relatively scarce in the natural environment (0.0005%; 20th abundant element in the continental crust), arsenic is widely distributed over the globe (Gebreyowhannes, 2009). All over the world where arsenic contamination in groundwater and its potentially severe human health effects have been reported, the impact has been the highest in Bangladesh and the Bengal delta basin of West Bengal, India (Chowdhury et al., 2000; Mukhopadhyay et al., 2002). > 90% of the total groundwater in West Bengal is affected by arsenic contamination (Sanyal and Nasar, 2002). The contamination of water occurs due to the dissolution of minerals like arsenopyrites from parent materials, geochemical reactions, biological activities and/or from anthropogenic sources such as the leaching of manmade arsenic compounds from smelting of metal ores, and wood preservatives (Shevade and Ford, 2004). There are two chemical hypotheses, namely arsenopyrite oxidation hypothesis (Mandal et al., 1996) and ferric oxyhydroxide reduction hypothesis

(Bhattacharyya et al., 1997), which explains the widespread arsenic occurrence in the groundwater of Bengal delta basin and Bangladesh. The latter hypothesis proved more consistent according to some literature (Sanyal, 1999; Aziz et al., 2016). According to this hypothesis, anoxic condition of the aquifers caused the mobilization of arsenic from arsenic bearing minerals into the groundwater.

Buildup of arsenic in soil due to the use of contaminated groundwater for irrigation has led to a global environmental concern, especially for rice production and food security in South Asia (India and Bangladesh) (Das et al., 2008; Khan et al., 2009). In addition, drinking of arsenic contaminated groundwater is a direct health threat to the people in this region and other parts of the world (Liu et al., 2002; Ng et al., 2003; Das et al., 2011; Sarkar and Paul, 2016). Consumption of arsenic contaminated drinking water may cause kidney, urinary tract, liver, skin, and rectum cancers in humans (Pontius, 1994). Non-carcinogenic diseases related to arsenic exposure are hypertension, diabetes mellitus, cerebrovascular and cardiovascular systems, and dysfunction of respiratory system (Thomas et al., 2001).

Arsenic is dominantly present in soils in inorganic forms which are a

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function of redox potential and pH of the medium. Arsenate (As (V)) is the major arsenic species in surface water over the pH range of 5–12 (Zeng, 2004). Arsenite (As (III)) is mostly found under reducing conditions, and thus is the most dominant species in groundwater over the pH range of 2–9 (Zeng, 2004).

Anion exchange, adsorption, reverse osmosis, coagulation, co-precipitation and solvent extraction are commonly known methods for removing arsenic from aqueous systems (Mohan and Pittman, 2007; Jadhav et al., 2015; Shakoor et al., 2016; Vithange et al., 2017). Various adsorbents including activated carbon, biochar, agricultural and industrial byproducts, zeolite and clay minerals, metal oxides and hydroxides, nanomaterials and resins were reported to remove arsenic from contaminated water (Mohan and Pittman, 2007; Sharma et al., 2014). However, available technologies for removing arsenic from soils are very limited. Phytoremediation of As from soil could be carried out through plants such as *Pteris vittata* (Mandal et al., 2012, 2017; Fayiga and Saha, 2016; Niazi et al., 2016). Ghosh et al. (2012) used farm yard manure and compost to make chelation of arsenic with humate compounds and immobilize it in soils. While the influence of organic matter on the mobility and bioavailability of arsenic species are ambiguous (Suda and Makino, 2016; Wang et al., 2016), some inorganic amendments such as iron compounds, phosphates, alkaline compounds, gypsum, biosolid, red mud, fly ash and clay minerals were found effective in immobilizing As in soils (Lombi et al., 2004; Kumpiene et al., 2008; Miretzky and Cirelli, 2010; Lee et al., 2011; Lim et al., 2016). However, many of these materials are expensive and still do not have standard protocol of practical soil application.

Due to their low cost, worldwide distribution and superior physico-chemical properties (e.g., high specific surface area, ion-exchange capacity, mechanical stability and lamellar structure), clay minerals (with or without modification) have also found widespread research attention in the remediation of metals and metalloids in water and soil (Sarkar et al., 2012, 2013; Sun et al., 2013; Perelomov et al., 2016; Kumararaja et al., 2017). In addition, such materials are ideal for one-time use requiring no regeneration.

Clay minerals modified with different inorganic ions like Fe, Al, Ti, organic acids, mineral acids, polymers, surfactants and nanoparticles were found promising for As remediation in contaminated water (Li et al., 2007; Boddu et al., 2008; Doušová et al., 2009; Akpomie and Dawodu, 2016; Sarkar and Paul, 2016). Ti-pillared smectite was considered in the present investigation due to its high adsorption affinity towards arsenic in aqueous system as it forms a polyhydroxy stable complexation with arsenic. Similarly the Fe-exchanged smectite forms stable iron-arsenate which enhanced arsenic adsorption efficiency in aqueous system. However, use of these modified clay minerals for the adsorption of As in contaminated soils is still an underexplored area of research. There is an urgent need to develop cost-effective methods for the removal/immobilization of As in contaminated soils. Therefore, the present study aimed to prepare and characterize three different inorganically modified clay minerals (Fe-exchanged and Ti-pillared smectite, and phosphate-bound kaolinite), and compare their As adsorption behavior in contaminated water and soil.

2. Materials and methods

2.1. Chemicals and clay minerals

Potassium dihydrogen phosphate (KH_2PO_4), iron sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and other chemicals were of analytical grade and purchased from Merck Millipore, Mumbai, India. Sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$), and titanium chloride (TiCl_4) were purchased from Sigma-Aldrich Chemicals Pvt. Ltd., New Delhi, India. The As stock solution (1000 mg L^{-1}) was prepared using $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in 0.01 M CaCl_2 in double distilled water. The working solutions of As were freshly prepared by diluting the stock solution in 0.01 M CaCl_2 solution.

0.1 N HNO_3 and 0.1 N NaOH were used to adjust the pH of As solutions as necessary.

The smectite and kaolinite samples in the form of bentonite and kaolin were purchased respectively from S D Fine-Chem Limited, Mumbai, India and Molychem, Mumbai, India. The clay samples contained 88% smectite (kaolinite and quartz as impurities) and 86% kaolinite (Fe-oxides and quartz as impurities), respectively, as the main mineral composition. The average particle size of unmodified, Fe-exchanged and Ti-pillared smectite was 158.10, 169.30 and 174.60 nm, respectively, while these values were 189.40 and 171.70 nm, respectively, for unmodified and phosphate-bound kaolinite. In order to reduce the cost of production, the raw materials were used as received without any purification.

2.2. Soil sample

Arsenic contaminated soil sample was collected (0–15 cm depth, order: Inceptisol) from Mitrapur, West Bengal, India (22.9981° N and 88.6121° E). The collected soil sample was air dried under shade and ground with mortar and pestle. The ground sample was passed through 2-mm sieve for further analysis purposes. The As content and other physico-chemical characteristics of the soil are given in Table 1.

2.3. Preparation of inorganically modified clay minerals

2.3.1. Preparation of iron-exchanged smectite

The smectite sample was treated with 0.1 M FeSO_4 solution in double distilled water (Te et al., 2015). In brief, 20 g of dried smectite was mixed with 200 mL of 0.1 M FeSO_4 in a 250 mL conical flask and stirred for 24 h in a mechanical shaker with a speed of 200 rpm at room temperature. The solid smectite was separated using centrifugation technique (4000 rpm for 5 min) and dried at 105°C for 24 h. The dried smectite sample was further heated to 350°C in a muffle furnace for 3 h and cooled to room temperature. Furthermore, the sample was washed with double distilled water until no reddish colour appeared upon addition of 1:10 phenanthroline (negative test for Fe) and dried at 60°C for overnight in a hot air oven.

2.3.2. Preparation of Ti-pillared smectite

At first, Na-smectite was prepared by adding 0.1 M NaOH drop by drop to a smectite suspension (10% w/v) under continuous stirring in a magnetic stirrer for 16 h. The saturated particles were separated through centrifugation (5000 rpm for 10 min) and washed with double distilled water until it became chloride free (no white precipitation upon the addition of a drop of 0.1 N AgNO_3 solution). Then Na-smectite was dried at 80°C for 4 h for further use. Ti-pillaring of Na-smectite followed the procedure of hydrolysis of TiCl_4 in reaction with HCl as described by Na et al. (2010). In short, 100 mL of TiCl_4 was dissolved in 200 mL of 3 M HCl solution under vigorous stirring for 2 h. The

Table 1
Physico-chemical properties of arsenic contaminated soil (Mitrapur, West Bengal, India).

Properties	Values
Clay (%)	26.5
Sand (%)	23.2
Silt (%)	50.3
Textural class	Silty clay loam
pH (1:2.5)	6.49
EC (dS m^{-1})	0.26
Organic carbon (g kg^{-1})	4.50
Amorphous Fe (%)	0.29
Total Fe (%)	1.31
Total As (mg kg^{-1})	14.1
Olsen extractable As (mg kg^{-1})	3.6
CEC [$\text{cmol (p}^+) \text{ kg}^{-1}$]	24.7

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