Arsenic adsorption on modified clay minerals in contaminated soil and water: Impact of pH and competitive anions

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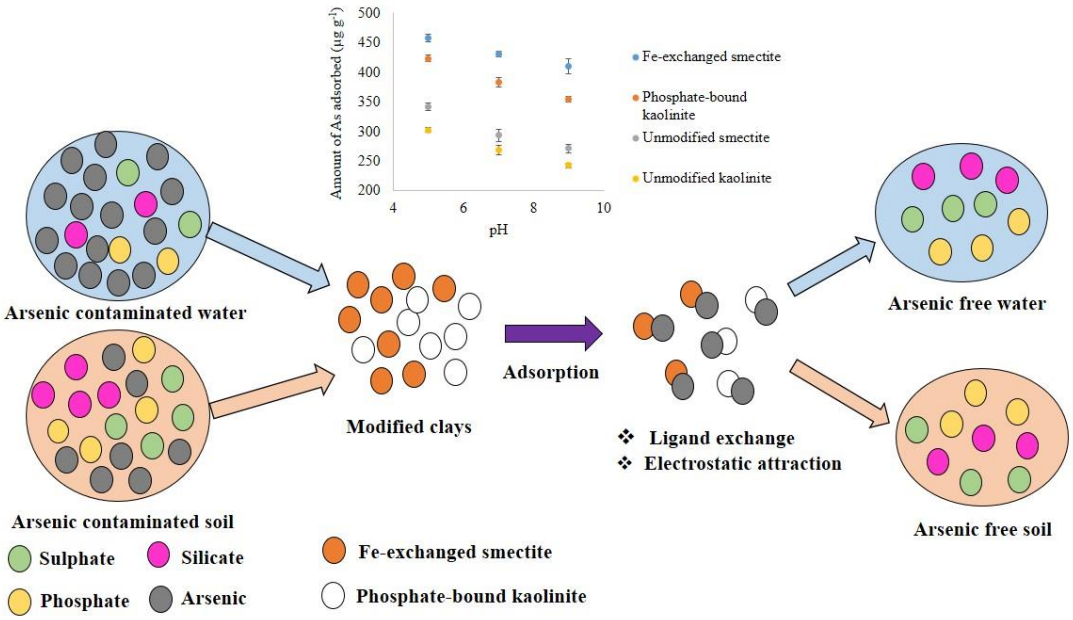
Abstract

This study evaluated the arsenic adsorption behaviour of Fe-exchanged smectite and phosphate-bound kaolinite, in soil, and aqueous systems of tap water and double distilled water in the presence of competing anions such as silicate, phosphate, and sulphate, and at variable pH values. The maximum amounts of As adsorbed in soil were 620.6 and 607.6 µg g^{-1} at pH 5 by Fe-exchanged smectite and phosphate-bound kaolinite, respectively. The pH-modified Freundlich equation fitted well ($R^2 > 0.96$) to the adsorption data, distinguishing the effect of pH on adsorption. The Freundlich constant values were $10^{1.69}$ and $10^{1.58}$ for Fe-exchanged smectite and phosphate-bound kaolinite, confirming a higher As-adsorption capacity of Fe-exchanged smectite than phosphate-bound kaolinite. The coefficients of pH-value were 0.004 and 0.005 for phosphate-bound kaolinite and Fe-exchanged smectite, suggesting that low pH was suitable for the adsorption. The As adsorption onto the adsorbents was decreased in tap water at low pH compared to the soil due to the presence of iron ($Fe^{2+/3+}$), sulphate, and bicarbonate in tap water. Among the competing anions in distilled water, phosphate was the most interfering anion for As adsorption. The competition coefficients of As-phosphate binary adsorption derived from the Sheindorf equation were 3.93 and 0.56 for Fe-exchanged smectite and phosphate-bound kaolinite at pH 5. The Fe-exchanged smectite thus can be used more effectively than phosphate-bound kaolinite for As remediation in systems having low pH (pH ~5) and high phosphate concentration.

Abbreviations: ICP-MS, inductively coupled plasma mass spectrometry; **NIST**, National Institute of Standards and Technology; **PZC**, point of zero charge; **WHO**, World Health Organization

Keywords: Arsenic, Competitive adsorption, Modified clays, pH, Soil and water remediation

Graphical abstract



Arsenic is one of the major contaminants in soil and water impacting millions of people worldwide. In this study, we evaluated two modified clays, namely Fe-exchanged smectite and phosphate-bound kaolinite, to remediate arsenic in contaminated soil and water under different pH conditions, and in the presence of competitive anions. We found that the Fe-exchanged smectite performed remarkably well in remediating soil and aqueous arsenic at low pH and high phosphate concentration.

1. Introduction

Arsenic (As) is one of the toxic contaminants present in soil and drinking water across the world, particularly in some densely populated areas of South Asia. The identified sources of As contamination in the environment include natural minerals (e.g., arsenopyrites), and biological and anthropogenic activities (e.g., metal smelting, wood preservation, pesticide synthesis, glass manufacturing, metal alloy, coal-fired power, and alternative medicine industries)[1]. In many countries (e.g., Bangladesh, India, Pakistan, Peru, Bolivia, Uruguay, Guatemala, Costa Rica, Mexico, Colombia, Chile), the range of As concentrations in groundwater (0.5–5000 µg L^{--1}) is notably higher than the World Health Organization (WHO) recommended safe limit (10 µg L^{--1})[2,3,4]. The As toxicity depends highly on its redox states and pH of the medium[5,6]. Among the species, arsenate (As(V)) is the most stable species in aerobic condition, while arsenite (As(III)) is predominant in anaerobic environments, and more toxic than As(V)[7]. Irrespective of the As species present in a contaminated soil or water system, significant research effort is needed to develop efficient but cost-effective methods to remediate the toxic element because it otherwise impacts lives of billions of people in Asia and elsewhere causing serious health issues including cancer.

Attempts to remove As species from aqueous solutions by various adsorbents showed a strong dependency of system

pH on the As removal efficiency of an adsorbent. For example, the maximum adsorption of As(III) and As(V) onto octahedral TiO_2 nanocrystals in aqueous systems appeared at pH values of 8 and 4, respectively [8]. Similarly, As(V) adsorption onto a surfactant modified zeolite was the maximum at pH 7, and no significant adsorption occurred below and above pH 7[9]. While a good number of studies previously reported [4,39] the effect of pH on As adsorption in aqueous media, only a limited literature is available on As adsorption[20,21] with varied pH range in the soil following the application of an As-immobilizing adsorbent. Soil is a heterogeneous medium, and as a result, As adsorption behaviour by an adsorbent following its application to the soil can be greatly different from that in an aqueous medium. Like soil pH, the presence of interfering anions, such as phosphate, molybdate, bicarbonate, and silicate, could play a crucial role in As adsorption in the soil solution. For example, Manning and Goldberg[10a] studied As(V) adsorption on different clay minerals such as kaolinite, montmorillonite and illite in the presence of phosphate and molybdate under different pH conditions, and found an inverse relationship between the amount of As adsorption and phosphate concentration. However, at an equimolar and ten times higher concentration of molybdate than phosphate, As adsorption decreased only slightly because maximum molybdate adsorption occurred at pH < 4 which was different from the optimum pH of As adsorption (pH 5.0 to 6.5 depending upon the clay mineral type)[10a]. Roy et al.[11] found that As(V) and molybdate adsorption was reduced in the presence of phosphate in soils due to competitive adsorption, but phosphate adsorption was not significantly decreased due to As(V) and molybdate. Manning and Goldberg[10b] further evaluated the effect of pH and competing ions (phosphate and molybdate) on As adsorption on oxide minerals such as gibbsite and goethite. On both the oxides, equimolar phosphate concentration decreased As(V) adsorption within the pH range of 2 to 11, but molybdate decreased As(V) adsorption below pH 6 only[10b]. Similarly, Jain and Loeppert[12] reported that phosphate significantly reduced the As(V) and arsenite adsorption onto ferrihydrite, depending on the pH and phosphate concentration of the system. Later on, Rong et al.[13] reported that organic ligand such as citrate decreased As(V) adsorption at acidic pH in an adsorbate concentration ranging between 0.006–0.27 mmol L^{--1}, but it remained unaffected at alkaline pH range. Nevertheless, literature is scarce about the influence of pH and competing anions such as silicate, phosphate and sulphate on the adsorption behaviour of As for its aqueous or soil phase remediation, especially when clay mineral-based amendments are applied.

Due to inexpensiveness, eco-friendliness, wide natural availability, and superior physicochemical properties (e.g., high specific surface area, high ion exchange capacity and fast reactivity), clay minerals (pristine or functionalized) have received widespread acceptance for heavy metal(loid)s remediation in contaminated water and soil[14,15,16]. Clay modification can be achieved in easy steps using agents such as polymers, inorganic salts, different acids, surfactants and nanoparticles, bestowing desired surface charge characteristics of raw clay minerals for bulk contaminant adsorption[17,18,19]. Clay mineral-based amendments such as organobentonite[20], Fe-exchanged smectite and phosphate-bound kaolinite[21], FeOOH-modified clay[17], and inorganic salts (Fe, Al, and Mn) treated kaolinite and montmorillonite[22] were reported to immobilize As in soils and water through enhanced adsorption. However, most of these studies were conducted under variable pH in water system only and did not provide any mechanistic insight on As removal in the presence of other competing anions. Furthermore, limited studies are available on the As adsorption behaviour of modified clays under variable pH levels in soil. The As adsorption behaviour onto modified clays in soil and water under varying levels of pH and competing anions is still poorly understood.

In view of the above, the present study aims to characterize the As adsorption behaviour onto two modified clay minerals (Fe-exchanged and phosphate-bound kaolinite) under varying level of pH and competing anions (silicate, phosphate and sulphate) in contaminated soil and water.

2. Materials and methods

2.1 Reagents and clay minerals

Potassium dihydrogen phosphate (KH_2PO_4), iron sulphate heptahydrate ($FeSO_4 \cdot 7\ H_2O$), sodium silicate (Na_2SiO_3), sodium chloride (NaCl), calcium chloride dihydrate ($CaCl_2 \cdot 2\ H_2O$), sodium sulphate (Na_2SO_4), sodium phosphate (Na_2HPO_4) and other chemicals were of analytical grade, and purchased from Merck Millipore, Mumbai, India. Sodium arsenate heptahydrate ($Na_2HAsO_4 \cdot 7\ H_2O$) was purchased from Sigma-Aldrich Chemicals, New Delhi, India. The As stock solution (1000 µg mL^{--1}) was prepared using $Na_2HAsO_4 \cdot 7\ H_2O$ in 0.01 M $CaCl_2$ in double distilled water. Laboratory tap water was also used as a solvent to prepare 1000 µg mL^{--1} As stock solution for investigating As adsorption in tap water under different pH conditions.

The smectite and kaolinite samples in the form of bentonite and kaolin clays were purchased respectively from SD Fine-Chem, Mumbai, India, and Molychem, Mumbai, India, and used without any purification treatment.

2.2 Preparation of Fe-exchanged smectite and phosphate-bound kaolinite

The details of the preparation procedure of Fe-exchanged smectite (using $FeSO_4 \cdot 7\ H_2O$) and phosphate-bound kaolinite (using KH_2PO_4) are described in Mukhopadhyay et al.[21]. In brief, Fe-exchanged smectite was prepared by equilibrating the smectite sample with 0.1 M FeSO4 · 7 H_2O (solid/solution 1:10) for 24 h. After equilibration, the clay sample was further heated in a muffle furnace (350°C), centrifuged (4000 rpm), and oven dried (60°C) for obtaining the final modified clay product. The phosphate-bound kaolinite was synthesized by equilibrating the kaolinite clay mineral with 200 mg L^{--1} KH_2PO_4 (solid/solution 1:10). The modified kaolinite was obtained after separating the solid kaolinite clay mineral from suspension by centrifugation and oven drying (105°C). Successful modifications of the clay minerals and their physico-chemical characteristics were described by Mukhopadhyay et al.[21].

2.3 Location, collection and characterization of soil samples

A naturally As-contaminated surface soil sample was collected (0--15 cm) from Mitrapur (22.9981° N and 88.6121° E), West Bengal, India. The collected soil sample was air dried, ground, and sieved through a 2-mm sieve, and used for further analyses. The experimental soil was silty clay loam in texture having pH (soil/water suspension 1:2) of 6.49. The available and total As contents of the contaminated soil were 3.6 and 14.1 mg kg^{--1}, respectively. The contaminated soil was also rich in iron (total and amorphous Fe contents were 1.31 and 0.29%, respectively)[21].

2. 4 Effect of pH on As adsorption in soil

As-contaminated soil (1.5 g) was mixed with Fe-exchanged smectite and phosphate-bound kaolinite at 0.25% (w/w) application rate in 50 mL plastic centrifuge tubes. A 30 mL aqueous solution of As (10 to 50 µg mL^{--1}) was added to

the soil--clay mixtures. The suspensions were shaken for 24 h on an end-over-end shaker to reach equilibrium. The experiment was conducted in triplicate at 25°C at pH 5, 7 and 9 (adjusted with 0.1 N HNO_3 and 0.1 N NaOH). Two blank tests were conducted with soil (in the absence of clay products) and without soil (in the absence of both soil and clay products). The amount of As adsorbed by the modified clays (q_e) was calculated using the mass balance relationship given below:

$$q_e = (C_0 - C_e)\, V/m \quad (1)$$

where C_0 and C_e are the concentrations of As (µg mL^{-1}) at initial and equilibrium stage, respectively; V is the volume of As solution (mL); and m is the mass (g) of the adsorbent. At equilibrium, q_e is called as the equilibrium adsorption capacity (µg g^{-1}), and C_e was called the equilibrium concentration.

2.5 Effect of pH on As adsorption in tap water

Laboratory tap water was collected, and its chemical parameters were characterized (Table 1) before the adsorption experiment. The As content in the laboratory tap water was below detection limit. A 1000 µg mL^{-1} As stock solution was prepared by dissolving $Na_2HAsO_4 \cdot 7\ H_2O$ in experimental tap water. The initial 50 µg mL^{-1} As working solution was prepared by diluting the 1000 µg mL^{-1} As stock solution, and final volume of the solution was made up using the collected tap water. The modified and unmodified clays (1.5 g) were equilibrated with 50 µg mL^{-1} As solution (30 mL) (solid/solution 1:20) for 24 h on an end-over-end shaker. Rest of the procedure and conditions were maintained same as the above-mentioned soil experiment. The amount of As adsorbed onto different clays under different pH values were calculated using the mass balance relationship.

2.6 Competitive adsorption of As onto different clay adsorbents

A clay/binary solution ratio of 1:20 (m/v) was used with Fe-exchanged smectite, phosphate-bound kaolinite, and unmodified smectite and kaolinite for the competitive As adsorption experiments. Samples (1.0 g) were given in centrifuge tubes, and 20 mL of solution containing the solutes (binary solution of As and competing silicate, phosphate or sulphate anions) were added to it. The pH of the suspension was adjusted to pH 5, 7 and 9. Rest of the procedure and conditions were maintained same as the previous experiments. Here, the As and competing solute stock solutions (1000 µg mL^{-1}) were prepared using Na-based salts ($Na_2HAsO_4 \cdot 7\ H_2O$, Na_2SiO_3, Na_2HPO_4, Na_2SO_4) in 0.01 M NaCl in double distilled water. The different graded working concentrations of As and competing anions were prepared by diluting the stock solutions, and volume made up with 0.01 M NaCl as background electrolyte. The content of Si in the supernatant was measured by inductively coupled plasma mass spectrophotometry (ICP-MS; Perkin Elmer NexION 300X, USA), while phosphate and sulphate were measured on a UV-vis spectrophotometer (Model: 3000+, Labindia Analytical, India).

2.7 Analysis of As

The As content in various aliquots was analysed by ICP-MS (Perkin Elmer NexION 300X, USA). CertiPUR As 1,000 µg mL^{-1} standard solution (NIST H_3AsO_4 in HNO_3) purchased from Merck, Germany, was used for the analytical method. The As standards of 250, 500 and 1000 µg L^{-1} including a blank sample were used for the calibration and

checked in an interval of every ten samples to validate the analytical procedure.

2. 8 Theory

2.8.1 Conventional and modified Freundlich equation

The As adsorption data obtained through the adsorption experiments in soils under varying pH levels were fitted to both the conventional and pH-modified Freundlich equations to elucidate the pattern of As adsorption under different system pH values. The conventional Freundlich adsorption isotherm is represented below:

$$q = K\,C^{1/n} \quad (2)$$

where q is the amount of adsorbate adsorbed at equilibrium (μg g^{-1}), and C is the equilibrium concentration (μg mL^{-1}), and K and $1/n$ are the Freundlich constants. Here, K and n are constants for the given adsorbate and adsorbent at the process temperature.

Bolt and Van Riemsdijk[23] proposed that when a uniform soil pH occurs in a given one-dimensional soil profile under heterogeneous soil conditions, the chemical interactions of the above system can be described by a power exchange function for metal ions (M) as given below[23,24]:

$$S_M = K\,[M]^a\,[H]^b \quad (3)$$

where S_M is the adsorbed metal concentration (μg g^{-1}), [M] and [H] are equilibrium concentrations of the metal (μg mL^{-1}) and hydrogen ions (mole L^{-1}), and a and b are empirical constants. Hingston et al.[25] used the same equation for explaining the influence of pH on the adsorption of a weak acid anion like phosphate. Later, De and Datta[26] used this equation with some minor modifications for determining the adsorption of phosphate considering the different levels of pH in soils, and called it as a modified Freundlich equation.

The modified Freundlich isotherm is given below:

$$X/m = K\,[H]^a\,[C]^b \quad (4)$$

where X/m is the amount of As adsorbed on per unit mass of the modified clay mineral; $[H^+]$ and [C] are the hydrogen and As ions (arsenate in this case) equilibrium concentrations; K, a, and b are the empirical constants optimized by least square method.

The linear form of modified Freundlich isotherm can be expressed as:

$$\log(X/m) + a\,\mathrm{pH} = b\,\log C + \log K \quad (5)$$

2.8.2 Computation of competitive adsorption coefficients

The competitive adsorption coefficients were calculated by the linear form of the Sheindorf-Rebhun-Sheintuch equation for a Freundlich-type multicomponent system[11], and are expressed as Eqs. (6) and (7):

$$C_i/C_j = (\beta_i/C_j) - a_{ij} \quad (6)$$

$$C_j/C_i = (\beta_j/C_i) - a_{ji} \quad (7)$$

In the binary solute system, a competitive adsorption coefficient was obtained by plotting (β_i/C_j) as the abscissa, and C_i/C_j as the ordinate[27], where:

$$\beta_i = ((K_{fi}\,C_i)/(x/m)_i^j)^{n_i/(n_i - 1)} \quad \text{(Eq. 8)}$$

where $(x/m)^j_i$ is the amount of solute *i* adsorbed per weight of the adsorbent in the presence of a competing solute *j*, K_{fi} is the single-component Freundlich exponential term for solute *i*, n_i is the Freundlich exponential term, C_i and C_j are the equilibrium concentration of solute *i* (As and solute *j* (silicate, phosphate and sulphate anions). The coefficients (a_{ij} and a_{ji}) are the negatives of the numerical value of the *y*-intercept which goes up to 10 indicating maximum degree of competition. The coefficient a_{ij} denotes $a_{As\text{-}Si}$, $a_{As\text{-}P}$ and $a_{As\text{-}S}$, suggesting the degree of competition provided by silicate, phosphate and sulphate anions on As adsorption on modified clay adsorbents, while a_{ji} denotes $a_{Si\text{-}As}$, $a_{P\text{-}As}$, and $a_{S\text{-}As}$, indicating the degree of competition provided by As on adsorption of silicate, phosphate and sulphate on modified clay adsorbents (a_{ji}).

3. Results and discussion

3.1 Effect of pH on As adsorption by modified clays in soil

The effect of varying levels of pH (5, 7 and 9) on As adsorption behaviour by modified clays (Fe-exchanged smectite and phosphate-bound kaolinite) in contaminated soil are shown in Fig. 1a, b. An individual adsorption curve was obtained at each pH value and fitted well to the conventional Freundlich isotherm with coefficient of determination (R^2) value from 0.78 to 0.92. Both the modified clays displayed high As adsorption at low pH level (~5) in the contaminated soil. A decreasing trend of As adsorption was observed at high pH level (~9). Adsorption pattern of Fe-exchanged smectite and phosphate-bound kaolinite showed reverse breaks (discontinuity of the As equilibrium concentration) for pH 5 at 20.1 and 20.9 µg mL^{--1}, respectively, (Fig. 1a, b) in the soil, suggesting the formation of precipitates or binuclear complexes[21]. The phosphate adsorption also showed a similar trend in soil where phosphate equilibrium concentration decreased after reaching a saturation point due to binuclear complex formation[28]. As is also analogous to phosphorus; therefore, similar precipitation or binuclear complex formation might have occurred onto modified clays in the case of As due to heterogeneous nature of the soil (presence of different soil constituents, organic matter, and competing ions)[21,28]. The maximum and minimum amounts of As adsorbed by Fe-exchanged smectite were 620.6 and 495.4 µg g^{--1} at pH 5 and 9, respectively. Similar trend was maintained by phosphate-bound kaolinite in the soil but adsorbed relatively less (607.6 and 497.0 µg g^{--1} at pH 5 and 9) amount of As compared to Fe-exchanged smectite. The maximum amount of As adsorption by the Fe-exchanged smectite under acidic pH could be explained by surface complexation mechanism due to higher affinity of Fe-exchanged smectite towards As and high surface positive charge on the adsorbent at low pH[10a, 29].

To explore the effect of pH on As adsorption by the modified clays in soil, the modified Freundlich equation was considered by taking into account the hydrogen ion (H^+) concentration in the process. The pH-modified Freundlich isotherm was obtained by plotting ($\log X/m + a \times \text{pH}$) against $\log C$, where *a* was the optimized value of H^+ concentration (Fig. 2a, b). Both the modified clays showed $R^2 > 0.95$ (Fig. 2 a, b), suggesting that As adsorption data closely fitted to the modified Freundlich equation. The higher the value of *K* (Fig. 2a, b), the higher was the adsorption of As in the contaminated soil. The *K* values were $10^{1.58}$ and $10^{1.69}$ for phosphate-bound kaolinite and Fe-exchanged smectite in soil, respectively. The *b* values were 0.96 and 0.97 ($p < 0.05$) for phosphate bound kaolinite and Fe-exchanged smectite in soil, respectively. The *a* value of the pH-modified Freundlich model indicated that the As adsorption onto modified clays occurred at low pH. The adsorption mechanism in soil at low pH could also be

explained by the nature of amorphous materials present in the soil[26, 30]. The contaminated soil contained high amount of amorphous and total Fe contents (0.29 and 1.31%, respectively) which might have formed stable iron-arsenate species. The reason behind the higher adsorption of As at low pH (~5), especially on Fe-exchanged smectite, might be due to the prevalence of surplus positive charges and reactive adsorption sites on the modified clay surface[31, 32, 33]. Ramesh et al.[34] reported that polymeric Al/Fe species incorporated into the interlayer of montmorillonite clay mineral had increased the positive charge on the clay surface at low pH. They described the high adsorption of As(V) at low pH by point of zero charge (PZC). At pH < PZC, the adsorbents' surface probably became positively charged, whereas pH > PZC, the adsorbents became negatively charged. Because of surplus positive charge of the modified clay adsorbents at pH < PZC, the adsorbents attracted As ions, resulting in greater As adsorption at pH 5 in case of Fe-exchanged smectite which showed comparatively better adsorption capacity than phosphate-bound kaolinite. However, phosphate-bound kaolinite followed the ligand exchange (with $–OH^{--}$ ions on the edge of kaolinite) mechanism for As adsorption at same pH (~5) condition. As pH increased, the surface of the modified clay adsorbent became negatively charged, which resulted in decreased As adsorption. Similar trend was observed during adsorption of As(V) onto titanium dioxide[35] and activated alumina[36] when they were used as adsorbents.

3.2 Effect of pH on As adsorption in tap water

The As adsorption onto modified and unmodified clays in tap water under different pH conditions varied remarkably (Fig. 3). At low pH (~5), the As adsorption on each clay adsorbent was significantly high, while the degree of As adsorption was moderate and low under pH 7 and 9, respectively, indicating a diminishing trend of adsorption with increasing pH values. The Fe-exchanged smectite adsorbed maximum amount of As (458 µg g^{--1}) is followed by the phosphate-bound kaolinite (423 µg g^{--1}), unmodified smectite (341 µg g^{--1}), and unmodified kaolinite (302 µg g^{--1}) at low pH (~5). The amount of As adsorption by the Fe-exchanged smectite and phosphate-bound kaolinite was further lowered in tap water (458 and 423 µg g^{--1}, respectively) (Fig. 3) than in the soil (620 and 607 µg g^{--1}, respectively) at pH 5 (Fig. 1 a, b).

The presence of sulphate (SO_4^{2--}; 3.10 mg L^{--1}) and bicarbonate (HCO_3^{--}; 1.20 meq L^{--1}) (Table 1) played a vital role in reducing the As adsorption capacity of the modified clay adsorbents. It is reported that bicarbonate and sulphate could effectively reduce As immobilization and compete for the adsorption sites, and change the surface charge of the adsorbents[37, 38]. Divalent anions like sulphate had better affinity than the monovalent anions like chloride (Cl^{--}) in competing with the adsorption sites[39], and chloride was present in the current experimental tap water (27.5 mg L^{--1}). Most of the anions would be dominant at high pH (~9), where the combination of high pH and competing anions including OH^{--} jointly would reduce the As adsorption capacity of the clay adsorbents. The order of As adsorption by the clay adsorbents at pH 9 was Fe-exchanged smectite (410 µg g^{--1}) > phosphate-bound kaolinite (354 µg g^{--1}) > unmodified smectite (271 µg g^{--1}) > unmodified kaolinite (242 µg g^{--1}). In addition, the presence of Fe (0.11 mg L^{--1}) in tap water (Table 1) contributed to decreased As adsorption on the clay adsorbents[40, 41]. Therefore, high pH (~9) of the aqueous system and presence of competing anions (OH^{--}, HCO_3^{--}, and SO_4^{2--}) and cations ($Fe^{2+/3+}$) in tap water were the major factors for low As adsorption onto the modified clay adsorbents.

3.3 Competitive As adsorption in the presence of silicate, phosphate and sulphate anions

In case of Fe-exchanged smectite at pH 5 in aqueous system, the degree of competition for As--silicate (a_{ij}) and silicate--As (a_{ji}) was 2.95 and 0.05 (Table 2), though the competition was not significant. However, with corresponding values of 3.93 and 0.86, the competition for the As--phosphate (a_{ij}) and phosphate--As (a_{ji}) systems was significant. The competition for the As--sulphate system was negligible. Similarly, in the case of phosphate-bound kaolinite, only significant competition for the As--phosphate system was observed (a_{ij} = 0.56), while the phosphate--As competition was insignificant (Table 2). Furthermore, no significant competition was obtained between As--sulphate, As--silicate, and vice versa on phosphate-bound kaolinite. There was low competition between As and counter anions onto the unmodified smectite and kaolinite as well due to their poor adsorption capacity. The competition between the anions onto the modified clays was relatively less at neutral pH (pH ~ 7) compared to acidic pH (pH ~ 5). Only As--phosphate and As--silicate showed significant influence when adsorbing onto Fe-exchanged smectite (0.92 and 0.41; Table 3). Similar to pH 5, As--sulphate and vice versa did not show any competition at pH 7. Most of the competition between all the competitive anions and As onto Fe-exchanged smectite was negligible in neutral aqueous solution. However, the As--silicate (a_{ij} = 0.31; Table 3) competition onto the phosphate-bound kaolinite was significant at neutral solution. Highest competitive coefficient was obtained between As--phosphate interaction and vice versa at pH 7 in case of phosphate-bound kaolinite (0.98 and 2.14; Table 3). Similar trend of competition between As--phosphate in modified clays was also dominant at pH 9 (Fe-exchanged smectite: a_{ij} = 0.74 and a_{ji} = 2.70; phosphate-bound kaolinite: a_{ij} = 1.15 and a_{ji} = --0.39; Table 4).

The higher the magnitude of the coefficient, the higher is the interference of the latter (competing anions in the study) on the adsorption of the former anion like As. The value of the competitive coefficients also described the nature of competition, viz., the higher the value of the coefficients, the lesser the adsorption of ions in question (As) onto the adsorbent. In this study, phosphate showed significantly higher competition with As compared to other competing anions, while sulphate showed negligible competition with As irrespective of pH. The order of competition between As and other anions was: phosphate > silicate > sulphate. Hence, phosphate was the most responsible which decreased the As adsorption onto the modified clays. Similarly, Biswas et al.[40] revealed that phosphate was the most competitive anion for As(III) and As(V) adsorption onto ferrihydrite. They reported the following order of competing ions which greatly influenced As adsorption: PO_4^{3--} >> Fe(II) > H_4SiO_4 = HCO_3^{--}. Furthermore, even at equimolar concentration, the presence of phosphate considerably decreased As adsorption on Fe-oxides such as goethite and gibbsite[10b, 42].

Earlier, Meng et al.[43] studied the impact of bicarbonate, silicate and sulphate anions on As removal in aqueous systems using $FeCl_3$ as an adsorbent. The adsorption capacity of ferric hydroxide for As(V) and As(III) was reduced from 864 and 116 to 274 and 23 µg mg^{--1} Fe, respectively, at pH 6.8 in the presence of silicate. However, the sulphate anions did not interfere on the removal of As(III) and As(V), which corroborated with our results. Similarly, Roy et al.[11] evaluated competitive coefficient for As(V) adsorption with respect to molybdate and phosphate in soils. They revealed that phosphate was more responsible than molybdate on As(V) adsorption. Further, the interference of phosphate on As(V) adsorption was higher than the interference of As on phosphate adsorption in terms of competitive coefficients for all soils. In this study, irrespective of the pH levels, the value of competitive coefficients between As and phosphate (a_{ij}) and vice versa (a_{ji}) (Tables 2--4) indicated that phosphate was the most competitive anion for As, suggesting higher As concentration in the aqueous phase than adsorbed phase due to the presence of high phosphate

concentration in water[44].

4. Conclusions

Fe-exchanged smectite adsorbed relatively more As at low pH (~5) than at high pH (~9), which was confirmed by fitting the adsorption data to the pH-modified Freundlich equation. The Fe-exchanged smectite and phosphate-bound kaolinite adsorbed lesser As in tap water than in soil at low pH due to the presence of iron, sulphate and bicarbonate in the aqueous system. Among the competing anions, phosphate was the most dominant and responsible counter anion that inhibited As adsorption onto the modified clays irrespective of the pH levels. The degree of competition contributed by phosphate anion was relatively higher at low pH, while sulphate did not show any significant competition to As adsorption. This study indicated that Fe-exchanged smectite could be used effectively for As remediation in systems having low pH (~5) and high phosphate concentration. An effective green technology for As remediation in contaminated soil and water could be developed using the Fe-exchanged smectite because the adsorbent requires no toxic reagents for its synthesis, and generates no toxic end products.

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Conflict of interest

The authors have declared no conflict of interest.

Data Sharing Statement

All the data have been presented already in the manuscript. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figure legends

Fig. 1 Conventional Freundlich model of arsenic adsorption onto (a) Fe-exchanged smectite and (b) phosphate-bound kaolinite in contaminated soil at pH 5, 7 and 9.

Fig. 2 The pH-modified Freundlich model of arsenic adsorption onto (a) Fe-exchanged smectite and (b) phosphate-bound kaolinite in contaminated soil at pH 5, 7 and 9.

Fig. 3 Effect of pH on As adsorption onto different modified and unmodified clays in tap water (Conditions: initial As concentration 50 µg mL^{--1}, shaking time: 24 h, solid/solution 1:20)

Tables

Table 1. Chemical characteristics of laboratory tap water

Chemical parameter	Value
pH	7.53
Electrical conductivity (EC) (dS m^{--1})	0.31
Chloride (Cl^{--}) (mg L^{--1})	27.50
Sulphate (SO_4^{2--}) (mg L^{--1})	3.10
Calcium (Ca^{2+}) (meq L^{--1})	3.60
Magnesium (Mg^{2+}) (meq L^{--1})	1.80
Nitrate (NO_3^{--}) (mg L^{--1})	1.90
Sodium (Na^{+}) (mg L^{--1})	2.70
Phosphate (PO_4^{3--}) (mg L^{--1})	Nd
Bicarbonate (HCO_3^{--}) (meq L^{--1})	1.20
Iron (Fe^{2+}) (mg L^{--1})	0.11
Arsenic (mg L^{--1})	Nd

Nd, not detected

Table 2. Summary of competitive coefficients for binary-solute system at pH 5

Anions *i* and *j*/Modified clays	Fe-exchanged smectite		Phosphate-bound kaolinite		Unmodified smectite		Unmodified kaolinite	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}	a_{ij}	a_{ji}	a_{ij}	a_{ji}
As + Si	2.95	0.05	1.25	0.30	0.16	0.45	0.08	--4.20
R^2	0.11	0.41	0.22	0.36	0.46**	0.48**	0.44**	0.91**
As + P	3.93	0.86	0.56	--1.66	0.26	1.81	0.17	4.20
R^2	0.81**	0.62**	0.85**	0.85**	0.48**	0.92**	0.43**	0.21
As + S	0.11	--0.70	--0.48	--1.53	--2.57	--4.70	--0.62	--0.19
R^2	0.60**	0.62**	0.95**	0.44**	0.94**	0.99**	0.99**	0.78**

$n = 3$

** Significant at α = 0.05 significance level

Table 3. Summary of competitive coefficients for binary-solute system at pH 7

Anions *i* and *j*/Modified clays	Fe-exchanged smectite		Phosphate-bound kaolinite		Unmodified smectite		Unmodified kaolinite	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}	a_{ij}	a_{ji}	a_{ij}	a_{ji}
As + Si	0.41	--0.46	0.31	--2.20	0.47	--0.45	0.13	--4.35
R^2	0.82**	0.11	0.54**	0.86**	0.42**	0.62**	0.49**	0.72**
As + P	0.92	--1.03	0.98	2.14	1.90	1.70	0.06	1.30
R^2	0.98**	0.66**	0.64**	0.17	0.47**	0.85**	0.42**	0.11
As + S	--0.42	--1.90	--0.08	--2.2	--1.64	--4.20	--0.65	--1.79
R^2	0.98**	0.87**	0.55**	0.64**	0.99**	0.27	0.95**	0.70**

n = 3

** Significant at α = 0.05 significance level

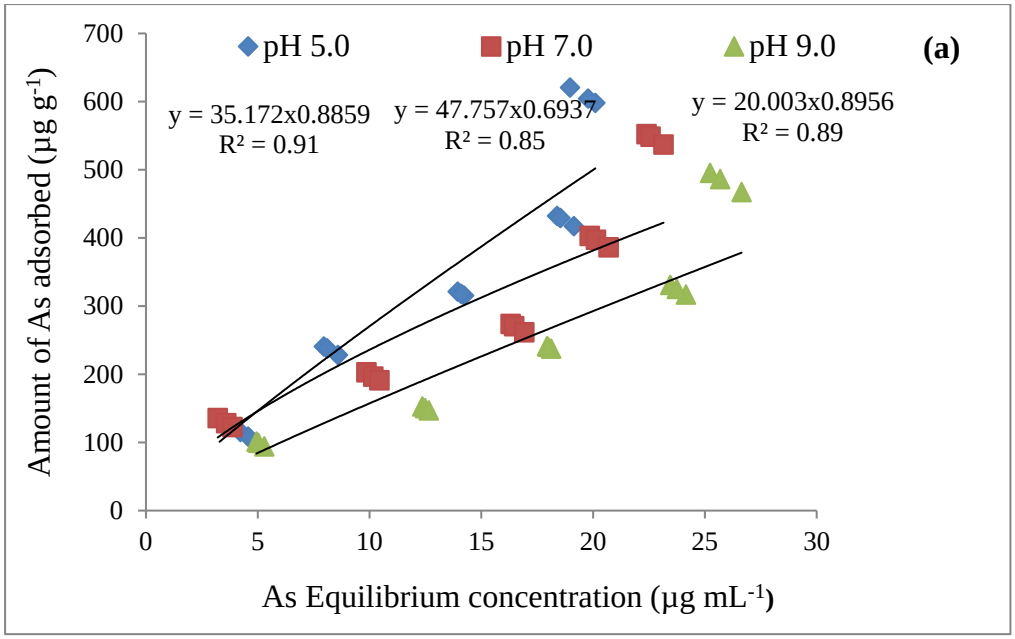
Table 4. Summary of competitive coefficients for binary-solute system at pH 9

Anions *i* and *j*/Modified clays	Fe-exchanged smectite		Phosphate-bound kaolinite		Unmodified smectite		Unmodified kaolinite	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}	a_{ij}	a_{ji}	a_{ij}	a_{ji}
As + Si	0.98	--12.12	0.64	--2.63	--1.51	2.21	--2.29	8.65
R^2	0.90**	0.34	0.49**	0.98**	0.81**	0.30	0.89**	0.01
As + P	0.74	2.70	1.15	--0.39	0.62	--7.62	--5.10	6.88
R^2	0.63**	0.82**	0.63**	0.96	0.46	0.75**	0.69**	0.09
As + S	--1.37	--3.39	--0.78	--14.92	2.65	2.11	2.33	9.81
R^2	0.75	0.99**	0.89**	0.15	0.30	0.29	0.98	0.02

n = 3

** Significant at α = 0.05 significance level

Figures



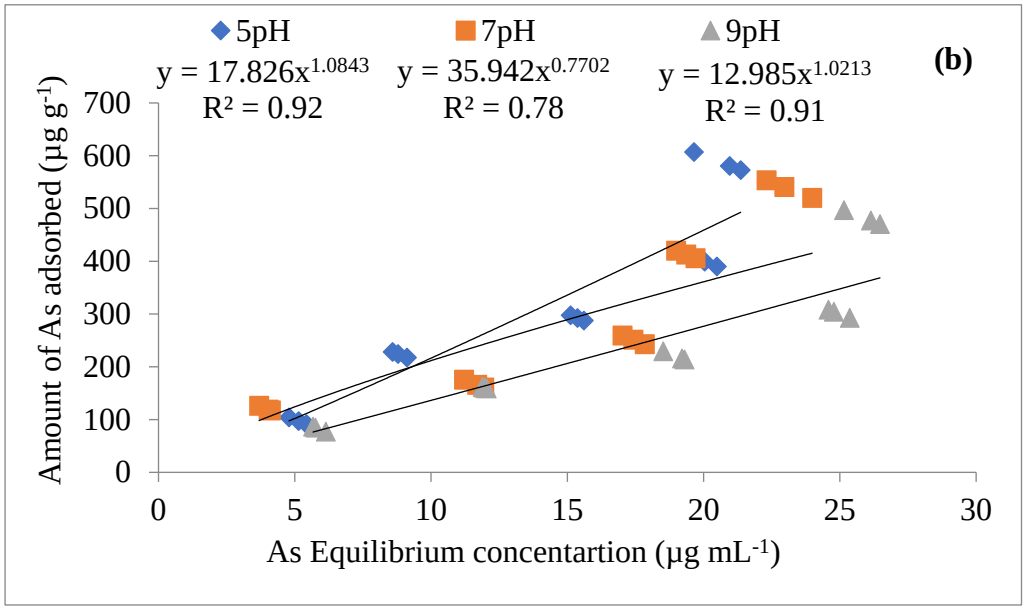


Fig. 1

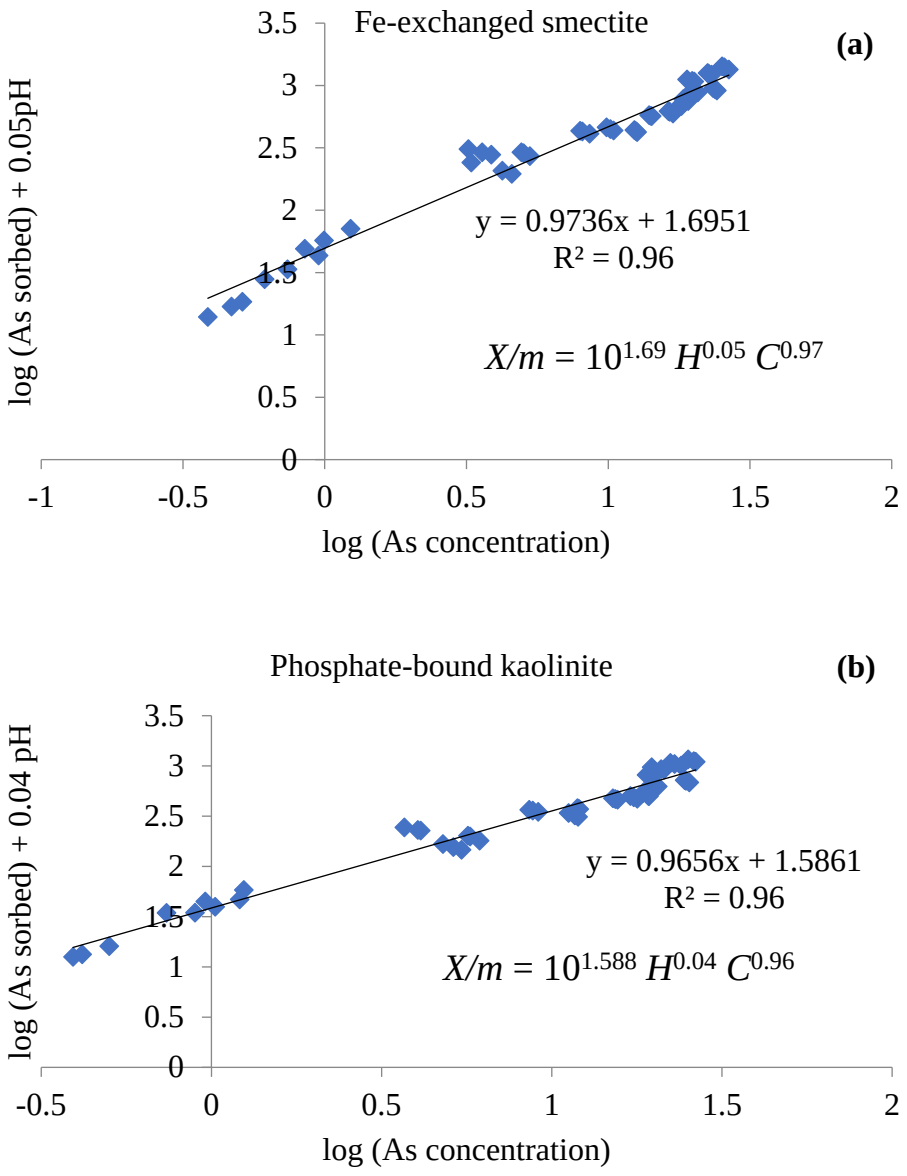

Fe-exchanged smectite
(a)
log (As sorbed) + 0.05pH
log (As concentration)
y = 0.9736x + 1.6951
R² = 0.96
X/m = 10^1.69 H^0.05 C^0.97
Phosphate-bound kaolinite
(b)
log (As sorbed) + 0.04 pH
log (As concentration)
y = 0.9656x + 1.5861
R² = 0.96
X/m = 10^1.588 H^0.04 C^0.96

Fig. 2

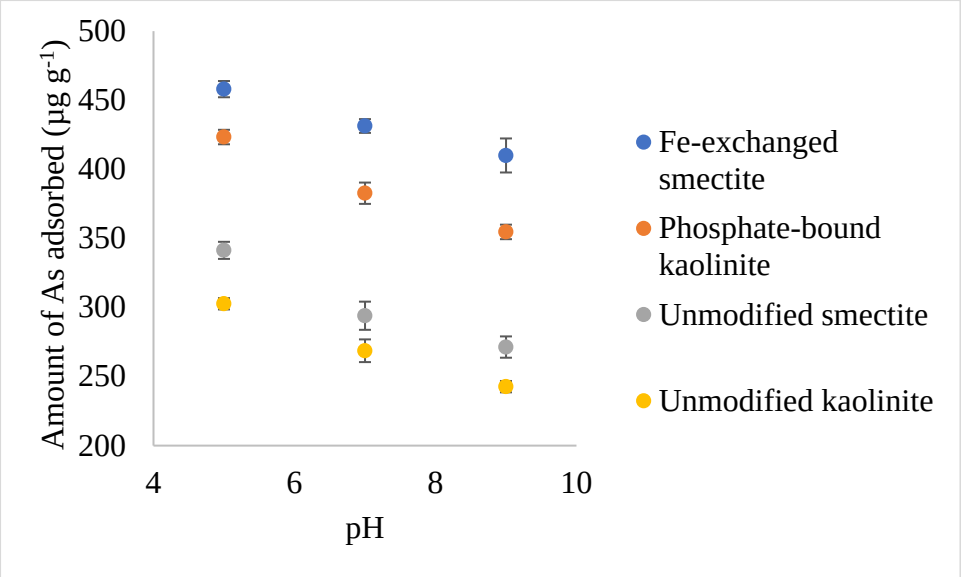

Amount of As adsorbed (µg g-1)
500
450
400
350
300
250
200
4
6
8
10
pH
Fe-exchanged smectite
Phosphate-bound kaolinite
Unmodified smectite
Unmodified kaolinite

Fig. 3