

Arsenic removal from real-life groundwater by adsorption on laterite soil

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Abstract

The adsorption characteristics of arsenic on laterite soil, a low-cost natural adsorbent, were studied in the laboratory scale using real-life sample. The studies were conducted by both batch and continuous mode. Laterite soil was found to be an efficient adsorbent for arsenic removal from the groundwater collected from arsenic affected area. The initial concentration of arsenic in the sample was 0.33 ppm. Under optimized conditions the laterite soil could remove up to 98% of total arsenic. The optimum adsorbent dose was 20 g/l and the equilibrium time was 30 min. Isotherm studies showed that the process is favorable and spontaneous. The kinetics showed that the removal of arsenic by laterite soil is a pseudo-second-order reaction. In the column study the flow rate was maintained at 1.49 m³/(m² h). Using 10 cm column depth, the breakthrough and exhaust time found were 6.75 h and 19.0 h, respectively. Height of adsorption zone was 9.85 cm, the rate at which the adsorption zone was moving through the bed was 0.80 cm/h, and the percentage of the total column saturated at breakthrough was 47.12%. The value of adsorption rate coefficient (*K*) and the adsorption capacity coefficient (*N*) were 1.21 l/(mg h) and 69.22 mg/l, respectively. Aqueous NaOH (1 M) could regenerate the adsorbent, and the regenerated adsorbent showed higher efficiency.

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1. Introduction

In many parts of India and Bangladesh the underground sources of drinking water are contaminated with arsenic. This causes nearly 100 million people to be affected by arsenic related diseases [1]. According to a current report, the adverse health effect caused by arsenic poisoning in this area are far more disastrous than any other calamity throughout the world in recent times. The genesis of arsenic pollution is not understood fully, yet it is thought that natural geological weathering is mostly responsible for the dissolved arsenic in groundwater. In many remote villages, arsenic contaminated tube-well is the only viable source for drinking water. In most cases excepting the presence of unacceptable level of arsenic, the groundwater is otherwise quite fit for drinking purpose. Thus a cost-effective

technique for arsenic removal providing a safe drinking water is an urgent need.

The maximum permissible limit of arsenic in India and Bangladesh is set to be 0.05 ppm, while according to USEPA and WHO guidelines it is 0.01 ppm. Report shows that the concentrations of dissolved arsenic in many existing wells providing drinking water exceed over 0.2 ppm.

The presence of arsenic in drinking water causes toxic and carcinogenic effects on human beings [1]. It is reported that long-term drinking of arsenic contaminated water causes gastrointestinal, skin, liver, and nerve tissue injuries. The toxicity of arsenic strongly depends on its oxidation state. It is reported that As(III) is more toxic than As(V) and organic arsenicals. Arsenate is more prevalent in oxygenated surface water while arsenite is more likely to occur in anaerobic groundwater [2,3]. Actual valence states depend, however, on the redox environment in water system and may vary from district to district. Thus finding out a technology for removing both forms of arsenic is a challenge. In many cases the adsorbent shows

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better efficiency for the adsorption of one form of arsenic [4,5].

The removal of As(III) from aqueous solution is usually more difficult compared to that of As(V), by almost all of the methods developed. It is because the predominant As(III) species is of neutral charge, while the As(V) species are negatively charged in the pH range of 4–10 [6]. So sometimes pre-oxidation step is required to convert As(III) to As(V) in order to achieve the removal of As(III). Various treatment methods such as ion exchange, adsorption, ultrafiltration, reverse-osmosis, and adsorption–coprecipitation by metals (predominately ferric chloride) followed by coagulation have so far been adopted for the removal of arsenic from aqueous media. In general, the removal of arsenic by precipitation is most effective for small quantities of highly concentrated arsenic containing waste. The most common arsenic removal method is precipitation–coagulation with lime and iron(III) salts followed by adsorption on to the resulting iron(III) hydroxide flocs [7]. However, the problems with this technique are the safe separation, filtration and handling of the contaminated coagulant sludge.

Much work has been done on arsenic removal through adsorption because the system is cost-effective and simple to operate. The effectiveness of adsorption-based methods depends primarily on the adsorbent used. So far, various adsorbents either from natural and synthetic origin have been developed for arsenic removal. These include metal-loaded coral limestone [8,9], hematite and feldspar [10], sandy soils [11], activated carbon [12,13], activated alumina [14,15], lanthanum-loaded silica gel [16], hydrous zirconium oxide [17], ferric hydr(oxides) [18], etc. In many such adsorption processes arsenate is removed more effectively than arsenite. Several iron(III) oxides, such as amorphous [19] and poorly crystalline [20] hydrous ferric oxide, and goethite (α -FeOOH) [21] are well-known to remove both As(III) and As(V) from aqueous solutions. Use of iron hydroxides either in the fine powdered or amorphous forms, however, requires follow-on solid/water separation with substantially added cost. Granular media used for arsenic adsorption include granular activated alumina [22] and granular activated carbon [23]. As it is easy to remove the adsorbent from the aqueous media after treatment, adsorption technique is generally considered to be a promising method. The cost effectiveness and the efficiency of the adsorbent for removing both forms of arsenic simultaneously is thus a challenge to the present day context.

It is understood that Fe(II)/Fe(III), Al(III), Cu(II), Mn(II), SiO₂ are mainly responsible for arsenic removal. Laterite soil is a red-colored clay-rich soil found in the tropics and subtropics. It needs high temperatures of the tropics and the abundant rainfalls to form. The water washes out the bases and the silicic acid, and enriches it with aluminium silicates, aluminium hydrosilicates, iron oxides and iron hydroxides. Especially the iron leads to the typical red color. The laterite soil occurs very widely in several districts (e.g. Purulia, Bankura and West Midnapore) of West Bengal (India). All these facts prompted the present investigators to evaluate the possibility of laterite soil to be used as a potential adsorbent for arsenic removal from the real sample. Studies were conducted in the laboratory scale by both batch and

column operations using real-life groundwater sample collected from the arsenic affected area. As far as our knowledge goes this is the first time when laterite soil is used for arsenic removal using real sample.

2. Materials and methods

2.1. Reagents

All chemicals used were of analytical reagent grade and were used without further purification. All aqueous solutions were prepared in double distilled water. The distilled water was examined for arsenic concentration. The concentration was lower than 0.01 ppm, the detection limit that can be easily achieved by the analytical methods used in this study [24,25]. The permissible limit of arsenic is 0.01 ppm.

Zinc fillings, concentrated HCl, SnCl₂·2H₂O, KI, Pb(OAc)₂·3H₂O (BDH, GPR), AgNO₃, sodium dodecyl sulfate (SDS) (all are from Merck) were used as received. Aqueous SDS (10⁻² M) and AgNO₃ (2 × 10⁻² M) solutions were used as stock. Stock solutions (10 ppm) of As(III) and As(V) were prepared using NaAsO₂ (Loba Chemicals) and Na₂HAsO₄·7H₂O (Nice Chemicals). Appropriately diluted solutions were made from the stock as and when required for calibration purpose.

2.2. Apparatus and instruments

All the apparatus used were soaked in concentrated HNO₃ for 12 h and then washed initially with tap water and then with distilled water. Then the apparatus were dried in hot air oven. Modified Gutzeit apparatus containing scrubber with lead acetate-soaked glass wool, and delivery L tube, were used for the production of AsH₃ gas. A digital pH meter (Orion, London) was used for all pH measurements. A high precision electrical balance (Sartorius GmbH) was used for weighing. All absorbance measurements were carried out with a spectrophotometer (Thermo Spectronic UV1, UK) equipped with 1-cm quartz cells. A mechanical shaker was used for shaking purpose. Gilson micropipette with disposable tips was used to add sample. Fe(III) and Al(III) concentrations were measured using atomic absorption spectrophotometer (Shimadzu AA-6650). Sorptomatic 1990 was used for BET analysis. JEOL JSM-5800 scanning electron microscope was used for SEM and EDX studies. Powder X-ray diffraction (XRD) pattern was recorded using a Philips PW-1710 model X-ray diffractometer and Cu K α radiation. The XRD data was analyzed by the X'Pert HighScore Philips analytical software.

2.3. Procedure

2.3.1. Preparation and characterization of adsorbent

In our work the locally available laterite soil, which is widely existent in several districts of West Bengal (the state where arsenic contamination is maximum), was used. The adsorbent was collected from Gopali area in West Midnapore. The material is the representative of the site chosen. The raw material did

Table 1
Characteristics and composition of laterite soil

| Properties | Quantitative value |
|-----------------------------------|--------------------|
| Geometric mean size (mm) | 0.164 |
| Bulk density (g/cm ³) | 2.5 |
| Surface area (m ² /g) | 15.365 |
| Pore volume (cm ³ /g) | 0.013 |
| Al (%) | 8.61 |
| Fe (%) | 52.05 |
| Si (%) | 35.04 |
| Cu (%) | 4.31 |
| pH _{zpc} | 6.96 |

not cost anything. SEM and EDX studies were performed on the soil to obtain the surface composition. The results are shown in Table 1. Laterite soil in various other places may have compositions varying but the major components Al, Fe, SiO₂ (and in some cases Cu) are the same. The mineralogical characterization of the laterite soil used in our studies was done using powder X-ray diffraction analysis and has been reported earlier [26]. The XRD pattern of the laterite soil reveals the predominance of the compounds such as aluminium iron silicon (Al_{0.7}Fe₃Si_{0.3}), silicon and aluminium copper (AlCu₃) based on the comparison of the standard and observed *d*-values. The X'Pert HighScore Philips analytical software was used for this purpose.

The adsorbent was made ready by the following procedure: first the soil was washed in tap water and dried under the Sun for 2–3 days. Then it was crushed and sieved to make the size of 0.164 mm. The soil was then washed thoroughly with tap water to remove the red color of iron, and finally it was washed with distilled water and dried in hot-air oven at 100 °C for overnight. This as-prepared particle was used for arsenic adsorption. The flow chart for the preparation of adsorbent (and also its use for arsenic adsorption) has been shown in Fig. 1. The specific surface area and pore volume of the soil was found out from the BET analysis. These values were 15.365 m²/g and 0.013 cm³/g, respectively. The pH_{zpc} of the material was 6.96.

2.3.2. Experimental studies

The real-life groundwater (tube-well water) was collected from Nivedita Palli, a severely affected area in Barasat situated in North 24 Paraganas (West Bengal, India). The composition of the water is shown in Table 2.

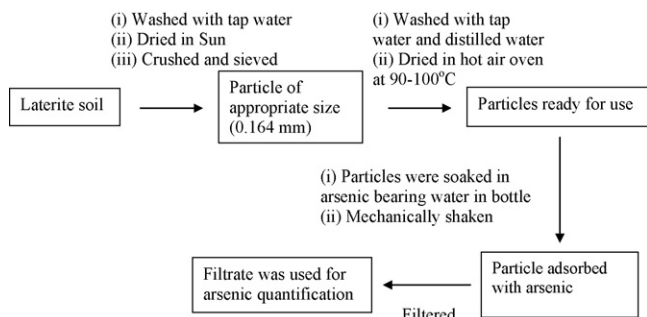


Fig. 1. The flow chart of the preparation procedure for the adsorbent and the removal of arsenic from aqueous media.

Table 2
Characteristics of real arsenic bearing groundwater

| Parameter | Quantitative value |
|------------------------|--------------------|
| pH | 7.2 |
| Turbidity (NTU) | 9 |
| Hardness (ppm) | 380 |
| Total iron (ppm) | 2.2 |
| Conductivity (μS) | 753 |
| TDS (ppm) | 378 |
| TOC (ppm) | 1.928 |
| Total alkalinity (ppm) | 213 |
| Phosphorus as P (ppm) | 2.42 |
| Silica (ppm) | 41.52 |
| Total arsenic (ppm) | 0.33 |

The batch experiments were performed at 25 ± 2 °C in a mechanical shaker at an agitation speed of 170 rpm. To find out the optimum adsorbent dose, arsenic bearing water (50 ml) with varying adsorbent doses (0–25 g/l) was shaken for 30 min. The optimum dose was found to be 20 g/l. The adsorption equilibrium time was found out using optimum adsorbent dose of 20 g/l and the shaking time was varied from 0 to 40 min. In all cases, after shaking, the samples were allowed to settle for 5 min, filtered through ordinary filter paper and the filtrate was used for the analysis of remaining arsenic in the solution.

Fixed-bed column study was conducted using a column of 2 cm diameter and 55 cm length. The column was packed with laterite soil and the depth was 10 cm (Fig. 2). The column was charged with arsenic bearing water in the up-flow mode with a volumetric flow rate of 1.49 m³/(m² h) (7.75 ml/min). The current flow rate was chosen to have sufficient amount of effluent water per hour for practical purpose. This range is also common for column design. The samples were collected at certain time intervals and were analyzed for the remaining arsenic concentrations.

2.3.3. Analytical methods

Total alkalinity, total hardness, phosphorus and silica were determined following the procedure described in standard methods of analysis [24].

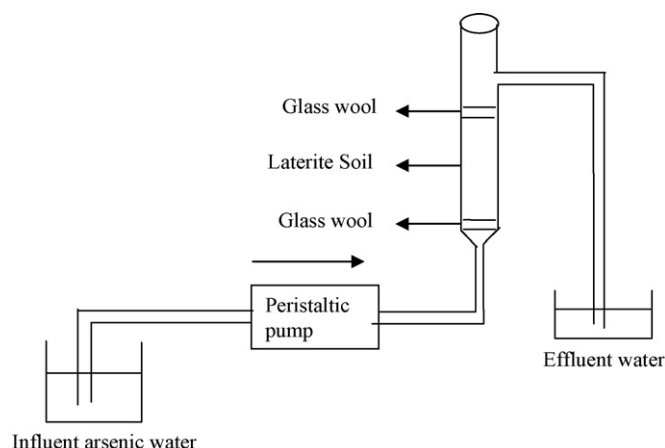


Fig. 2. Schematic diagram of fixed bed column.

Quantification of total arsenic was made using either the method developed in our laboratory (Method A) [25] or the standard silver diethyldithiocarbamate (SDDC) method (Method B) [24]. The two methods of analysis afforded comparable results. Both the methods are precise (S.D. $< \pm 5\%$), accurate (accuracy $< 10\%$) and sensitive (LOD: 0.02 ppm or less). But Method A is more users friendly and cost-effective. Thus while Method B requires CHCl_3 , which is a known carcinogen, and SDDC (a costly reagent) as the absorbing reagent, Method A involves AgNO_3 in aqueous SDS micelle. Method A is developed in our laboratory, and thus the analytical data were verified with standard SDDC method (Method B).

Method A: A reliable modified Gutzeit method has been developed for the determination of arsenic. For the quantification of total arsenic, 35 ml of the sample solution in the concentration range of 0–0.5 ppm was taken in the conical flask, and concentrated HCl (5.0 ml), KI (2.0 ml, 15%) and SnCl_2 (0.4 ml, 40%) were added successively. Then 30 min time was allowed for the reduction of As(V) to As(III). Addition of Zn fillings (~ 3 g) into it started producing AsH_3 gas immediately. The gas was passed through a scrubber containing $\text{Pb}(\text{OAc})_2$ -soaked glass wool to trap any H_2S gas formed. Finally the arsine gas was allowed to enter for 40 min into the reagent solution containing 2.05 ml of AgNO_3 (final concentration 4.87×10^{-4} M) in aqueous SDS micelle (10^{-2} M). The reagent solution turned yellow due to the formation of silver nanoparticle. The absorbance was measured at the λ_{max} : 395 nm against a blank produced from a solution containing 0 ppm of arsenic with the same experimental procedure. The color of silver sol was stable under ambient condition for > 6 h while kept in dark. The measurements were done within 2 h of the experiment.

Method B: The concentration of total arsenic was measured by standard silver diethyldithiocarbamate (SDDC) method. For each test 35 ml of sample was taken in a clean Gutzeit generator and to that solution were added concentrated HCl (5.0 ml), KI (2.0 ml, 15%) and SnCl_2 (0.4 ml, 40%) successively. Then 30 min time was allowed for the reduction of As(V) to As(III). In the mean time the glass wool in the scrubber was impregnated with six to eight drops of $\text{Pb}(\text{OAc})_2$ solution and 4.0 ml SDDC/ CHCl_3 /morpholine reagent was taken in the absorber tube. After 30-min reaction, 3.0 g zinc was added into the generator and immediately scrubber-absorber assembly was connected. The reaction was allowed to continue for another 30 min to ensure complete evolution of AsH_3 gas. It is also prescribed to heat the generator slightly to ensure that all arsine is released. The absorbance of the SDDC reagent was measured at 535 nm using the reagent blank as the reference.

3. Results and discussions

3.1. Batch adsorption experiments

3.1.1. Effect of adsorbent dose and contact time

Batch study was conducted to find out the optimum adsorbent dose and the contact time for maximum possible removal of the adsorbate. A series of 50 ml samples of arsenic bearing drink-

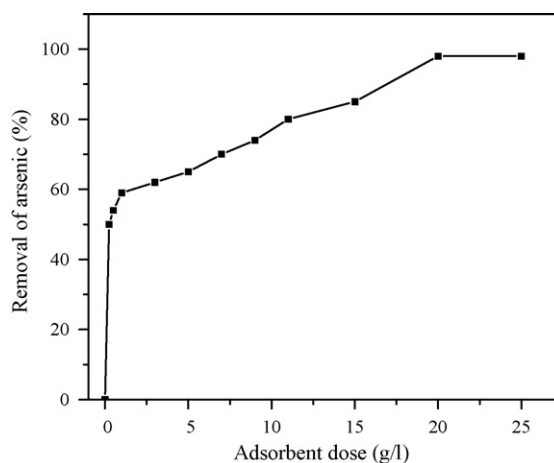


Fig. 3. Effect of dose variation.

ing water were shaken for 30 min with the varying adsorbent doses of 0–25 g/l. Studies showed that the arsenic removal efficiency was increased with increase of adsorbent dose (Fig. 3), and 20 g/l of that adsorbent could remove $\sim 98\%$ of arsenic. Thus the adsorbent dose 20 g/l was used for the entire study. With the dose of 20 g/l, the kinetic study was performed and it was observed that on 20-min shaking $\sim 95\%$ of total arsenic could be removed. With further shaking of another 10 min the arsenic removal reached at $\sim 98\%$ (Fig. 4). Thus a shaking time of 30-min is adopted as the equilibrium time.

3.1.2. Adsorption isotherm study

Langmuir and Freundlich isotherm studies were conducted in order to investigate the maximum adsorption capacity of laterite soil towards arsenic. The adsorbent dose was varied in the range of 0.25–20 g/l. The initial arsenic concentration of the sample was 0.33 ppm and the pH 7.2. Shaking speed 170 rpm, equilibrium time 30 min and temperature $25 \pm 2^\circ\text{C}$ was applied for the isotherm studies. The relation between the amount of adsorbate adsorbed by the adsorbent and the equilibrium concentration of the adsorbate can be expressed by the linearized Langmuir

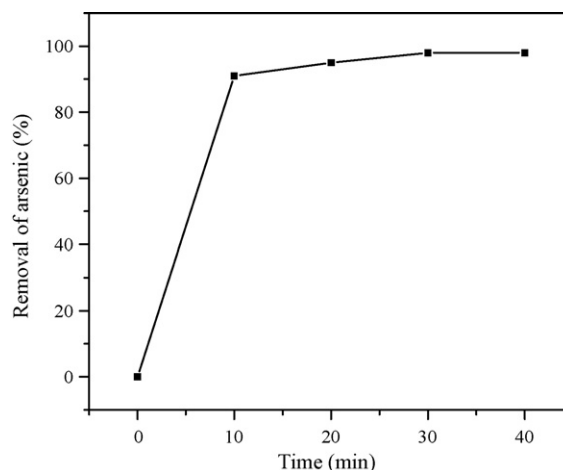


Fig. 4. Kinetic plot for the adsorption of arsenic on laterite soil.

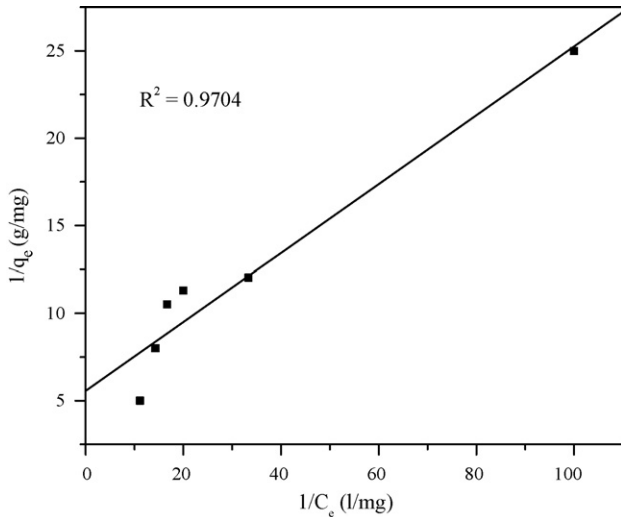


Fig. 5. Langmuir isotherm model for arsenic adsorption on laterite soil.

adsorption isotherm as

$$\frac{1}{q_e} = \frac{1}{Q_{\max}} + \frac{1}{bQ_{\max}} \left(\frac{1}{C_e} \right) \quad (1)$$

and the Freundlich isotherm as

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (2)$$

where q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent, b the adsorption constant related to the enthalpy of adsorption, C_e the equilibrium concentration of arsenic, Q_{\max} the maximum adsorption capacity, and n and k_f are the constants depending upon the nature of the adsorbate and adsorbent where n represents the adsorption intensity and k_f represents the adsorption capacity. Linear Langmuir isotherm was drawn (Fig. 5) by plotting $1/q_e$ versus $1/C_e$, and the linear equation obtained is $1/q_e = 0.1968 (1/C_e) + 5.5630$ (with correlation coefficient $R^2 = 0.9704$). The maximum adsorption capacity (Q_{\max}) found was 0.18 mg/g. Freundlich isotherm for the adsorption was drawn (Fig. 6) by plotting $\ln q_e$ versus $\ln C_e$, and the equation obtained is $\ln q_e = 0.6251(\ln C_e) - 0.3838$ (with correlation coefficient $R^2 = 0.9407$). It is observed from the curves and the correlation coefficient data that the adsorption follows neither Langmuir isotherm nor Freundlich isotherm in a perfect way. This is possibly because the real water contains both As(III) and As(V), and at the sample water pH both As(III) and As(V) can exist as various species (ionic or neutral). As a result the adsorption follows a mixed model.

Langmuir and Freundlich isotherms do not explain the adsorption mechanism. In order to get the idea about the type of adsorption the data were applied to Dubinin–Radushkevich (D–R) isotherm [27,28], which can be expressed as

$$\ln Q = \ln Q_m - k\varepsilon^2 \quad (3)$$

where ε (Polanyi potential) can be expressed as: $\varepsilon = RT \ln[(1 + (1/C_e))]$. In the above expression Q is the amount of arsenic adsorbed (mg/g) at equilibrium per unit weight of adsorbent, Q_m the maximum adsorption capacity (mg/g), C_e the

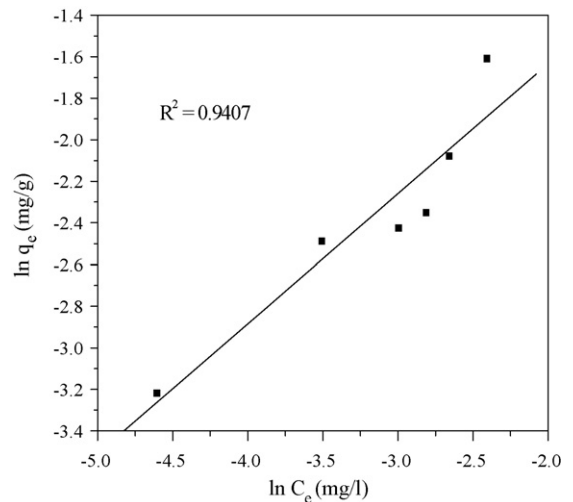


Fig. 6. Freundlich isotherm model for arsenic adsorption on laterite soil.

equilibrium concentration of arsenic in the solution (ppm), k the constant related to adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$), R the universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). D–R isotherm was drawn by plotting $\ln Q$ against ε^2 (Fig. 7). Q_m and k were calculated from the slope and the intercept of the graph, and found to be 0.17 mg/g and $0.0108 \text{ mol}^2 \text{kJ}^{-2}$, respectively, where k was independent of temperature. The mean free energy of adsorption (E), defined as free energy change when 1 mol of ion is transferred from infinity in solution to the surface of the solid, was calculated from the k -value using the following equation:

$$E = -(2k)^{-0.5} \quad (4)$$

The magnitude of E is useful for estimating the type of adsorption. If this value is in the range of $8\text{--}16 \text{ kJ mol}^{-1}$, the adsorption type is ion exchange [29], and if it is $\leq 8 \text{ kJ mol}^{-1}$, then the adsorption is physical (due to weak van der Waals force). The value of E found in this study was 6.8 kJ mol^{-1} . This indicates that the adsorption is physical in nature.

In order to predict the adsorption efficiency of the process and to know whether the process is favorable or unfavorable for the

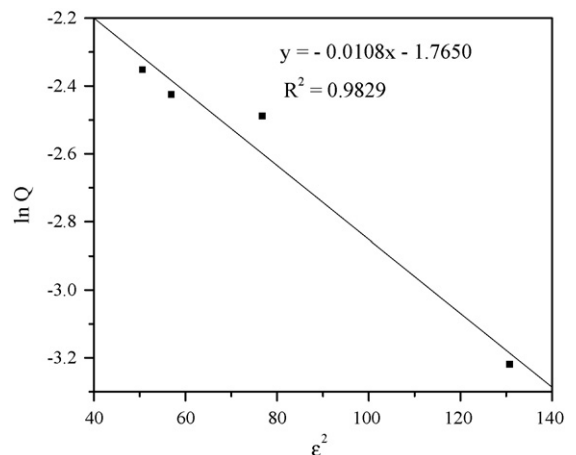


Fig. 7. D–R isotherm model for arsenic adsorption on laterite soil.

Table 3
Constant values of Langmuir, Freundlich, and D–R isotherm

| | |
|-----------------------------|---------|
| Temperature (K) | 298 ± 2 |
| Langmuir isotherm | |
| Q_{\max} (mg/g) | 0.18 |
| b (l/mg) | 28.23 |
| R^2 | 0.9704 |
| Freundlich isotherm | |
| n | 3.68 |
| k_f | 0.682 |
| R^2 | 0.9407 |
| D–R isotherm | |
| E (kJ mol ⁻¹) | 6.80 |
| Q (mg/g) | 0.17 |
| R^2 | 0.9829 |
| R_L | 0.099 |

Langmuir type adsorption, the isotherm shape can be classified by a term R_L , a dimensionless constant separation factor, which is defined by the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where C_0 is the initial concentration of arsenic (ppm) and b is the Langmuir isotherm constant. Value of $R_L < 1$ represents favorable adsorption and $R_L > 1$ represents unfavorable adsorption [27]. The constant values of all isotherms are shown in Table 3. In our case the value of R_L is 0.099, which suggests that the adsorption is favorable. Furthermore, the standard Gibbs free energy changes (ΔG°) for the adsorption process can be calculated by using the following equation:

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^\circ}{RT} \quad (6)$$

where b (Table 3) is the Langmuir isotherm constant, R the universal gas constant (8.3145 J mol⁻¹ K⁻¹), and T is the absolute temperature. The calculated ΔG° value is -8.30 kJ mol⁻¹. The negative ΔG° value indicates that the adsorption is spontaneous.

3.1.3. Adsorption kinetics

In batch experiments, kinetic study is very important to find out the contact time of the adsorbent with adsorbate and for evaluating reaction coefficients. In order to investigate the mechanism of arsenic adsorption onto the laterite soil, four kinetic models, viz., first-order reaction model [30] based on the solution concentration, pseudo-first-order equation of Lagergren et al. [31] based on the solid capacity, second-order reaction model based on the solution concentration and pseudo-second-order reaction model of Ho and McKay [32] based on the solid phase sorption were analyzed and a comparison of the best fit sorption mechanism were made.

3.1.3.1. First-order reaction model. First-order rate equation based on the solution concentration can be represented as

$$-\frac{dC_t}{dt} = k_1 C_t \quad (7)$$

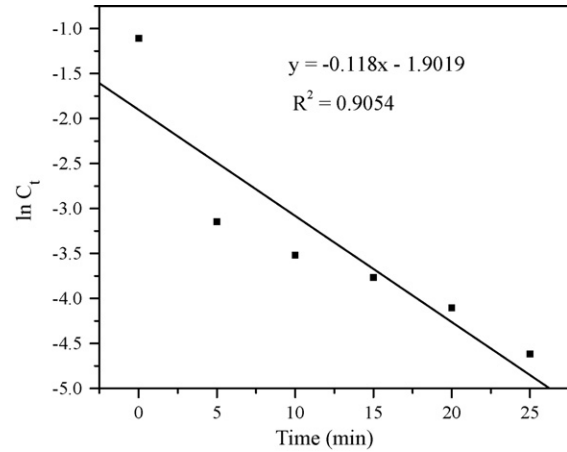


Fig. 8. Linear model of first-order reaction kinetics.

Rearranging Eq. (7):

$$-\frac{dC_t}{C_t} = k_1 dt \quad (8)$$

Integrating Eq. (8) for the boundary conditions $t=0$ to $t=t$ and $C_t=C_0$ to $C_t=C_t$ gives the form:

$$\ln C_t = \ln C_0 - k_1 t \quad (9)$$

So Eq. (9) dictates that a plot of $\ln C_t$ versus t indicates the linear plot of first-order equation. Fig. 8 shows the plot of $\ln C_t$ versus t . A best-fit line was drawn and the correlation coefficient (R^2) was found to be very poor (0.9054), which indicates that the adsorption did not follow the first-order reaction model.

3.1.3.2. Pseudo-first-order reaction model. The pseudo-first-order kinetic model based on the solid capacity for sorption analysis is of the form:

$$\frac{dq_t}{dt} = k_{s1}(q_1 - q_t) \quad (10)$$

Integrating Eq. (10) for the boundary condition $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ gives the linearized form as shown by following equation:

$$\ln(q_1 - q_t) = \ln(q_1) - k_{s1} t \quad (11)$$

Therefore from Eq. (11) it can be inferred that a linear plot of $\ln(q_1 - q_t)$ versus t indicates the reaction to be of pseudo-first-order (Fig. 9). The correlation coefficient of the linear fit indicates ($R^2 = 0.9238$) that the adsorption did not follow the pseudo-first-order reaction model.

3.1.3.3. Second-order reaction model. Second-order rate equation is widely used for metal ion adsorption, and can be mathematically represented as

$$-\frac{dC_t}{dt} = k_2 C_t^2 \quad (12)$$

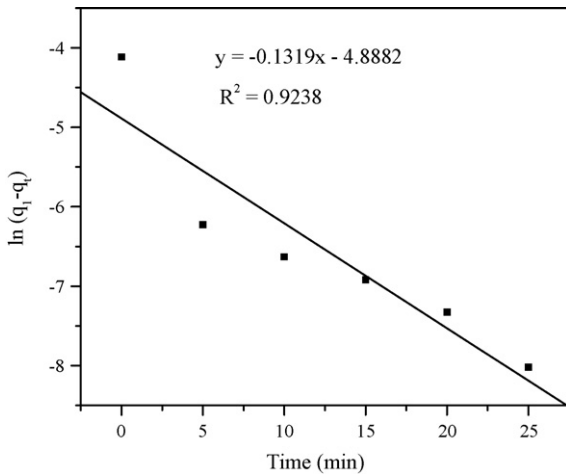


Fig. 9. Linear model of pseudo-first-order reaction kinetics.

Rearranging Eq. (12) and integrating for the boundary condition $t=0$ to $t=t$ and $C_t=0$ to $C_t=C_t$ we get:

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2t \quad (13)$$

According to Eq. (13) a linear plot of $1/C_t$ versus t with good correlation coefficient indicates that the reaction rate is of second-order. A plot of $1/C_t$ versus t for the adsorption under consideration is shown in Fig. 10. The correlation coefficient ($R^2 = 0.9646$) indicates that the adsorption followed the second-order reaction model in a better way than the first-order and pseudo-first-order reaction model.

3.1.3.4. Pseudo-second-order reaction model. A pseudo-second-order expression based on the adsorption equilibrium capacity may be expressed as

$$\frac{dq_t}{dt} = k[q_e - q_t]^2 \quad (14)$$

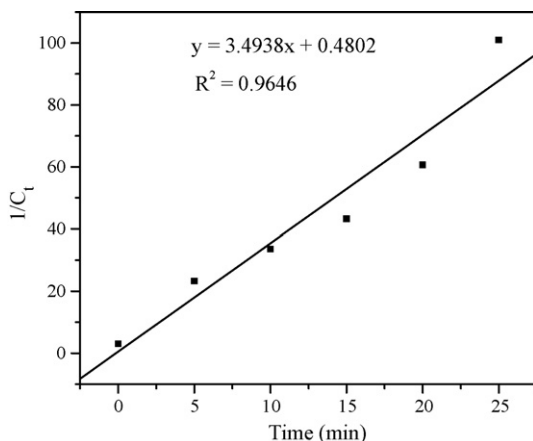


Fig. 10. Linear model of second-order reaction kinetics.

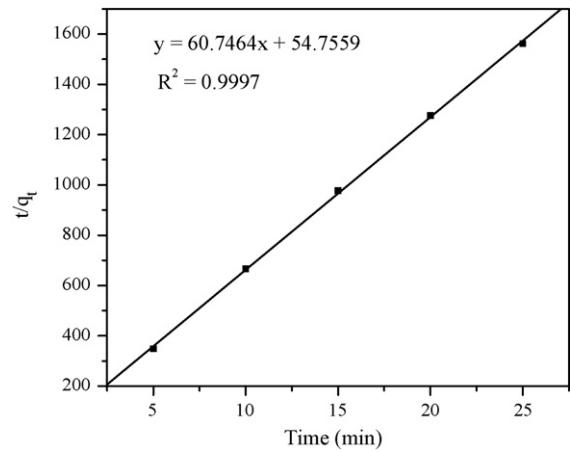


Fig. 11. Linear model of pseudo-second-order reaction kinetics.

Rearranging Eq. (14) and integrating the obtained equation for the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ we get:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (15)$$

which is the integrated rate law for a pseudo-second-order reaction.

Rearranging Eq. (15) we get:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \quad (16)$$

where $h = kq_e^2$. Eq. (16) indicates that a linear plot of t/q_t versus t confirms that the reaction rate follows pseudo-second-order kinetics. Fig. 11 shows the plot for pseudo-second-order model. The linear fit (correlation coefficient, $R^2 = 0.9997$) indicates that the adsorption follows the pseudo-second-order model best.

3.1.4. Studies on the kinetic parameters

In the adsorption process, the rate of reaction is of prime importance and the rate-limiting step will greatly aid the selection of adsorber configuration and also the time of contact to be allowed between sorbent and sorbate. To interpret the experimental data properly, it is necessary to determine the steps in the adsorption process, governing the overall removal rate for the system. Also, the rate-limiting step is important in the field application point of view. The rate-limiting step of the adsorption process can be calculated using the first-order kinetic data [33–35]. Assuming the spherical geometry of the adsorbent, the first-order rate constant, k_1 obtained from the slopes of the straight lines of first-order model can be utilized to estimate the pore diffusion coefficient as defined in Eq. (17) or the film diffusion coefficient as defined in Eq. (18):

$$t_{1/2} = 0.030 \times \frac{r^2}{D_p} \quad (17)$$

$$t_{1/2} = 0.23 \times \frac{r\delta}{D_f} \frac{C_s}{C_e} \quad (18)$$

Eqs. (17) and (18) are called half-time equations where r is the mean geometric radius of the adsorbent in cm, δ the thickness of

Table 4
Constant values of the pore diffusion and film diffusion models

| | |
|--|--------|
| Initial concentration (ppm) | 0.33 |
| C_e (ppm) | 0.01 |
| k_1 ($\times 10^{-3} \text{ s}^{-1}$) | 1.52 |
| $t_{1/2}$ ($\times 10^{-3} \text{ s}$) | 0.456 |
| r (cm) | 0.0082 |
| D_f ($\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) | 1.32 |
| D_p ($\times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) | 4.42 |

the water film adhered to the adsorbent in cm, D_p and D_f are the pore and film diffusion coefficients, respectively in $\text{cm}^2 \text{ s}^{-1}$, C_s and C_e are the concentrations of the adsorbate on the adsorbent and in the solution at equilibrium, respectively in mg/g and mg/l, respectively. The $t_{1/2}$ is the time required to bring down the adsorbate concentration to half the initial concentration in s.

Asher and Pankow [36] suggested a relationship between $t_{1/2}$ and k_1 (overall reaction rate constant) to obtain $t_{1/2}$ values as

$$t_{1/2} = -\frac{\ln(0.5)}{k_1} \quad (19)$$

$t_{1/2}$ values can be calculated from Eq. (19) and by substituting $t_{1/2}$ values in Eqs. (17) and (18), the D_p and D_f values can be calculated for initial arsenic concentration of 0.33 ppm assuming $\delta = 0.001 \text{ cm}$. The values obtained are presented in Table 4. According to Michelson et al. [34], for the film diffusion to be the rate-limiting step, the value of film diffusion coefficient (D_f) should be in the range of 10^{-6} to $10^{-8} \text{ cm}^2/\text{s}$, and for the pore diffusion to be the rate limiting, the pore diffusion coefficient (D_p) should be in the range of 10^{-11} to $10^{-13} \text{ cm}^2/\text{s}$ for the heavy metals. In the present case film diffusion appears to be the rate-limiting step as is evidenced from Table 4.

3.2. Fixed bed column for arsenic removal

The efficiency of the treatment technique depends on arsenic concentration and species in source water and other constituents in the water. Fixed bed column study was conducted with real arsenic bearing groundwater using a column of 2 cm diameter and 55 cm length. The column was packed with laterite soil and the depth was 10 cm. The column was charged with arsenic bearing water in the up-flow mode with a volumetric flow rate of $1.49 \text{ m}^3/(\text{m}^2 \text{ h})$ (7.75 ml/min). The breakthrough curve is shown in Fig. 12. The breakthrough time (corresponding to $C/C_0 = 0.030$) and exhaust time (corresponding to $C/C_0 = 0.9$) were found to be 6.75 h and 19.0 h, respectively. The corresponding volumes of the arsenic bearing water treated were 3.135 l and 8.835 l, respectively. The height of adsorption zone was found to be 9.85 cm and the rate at which the adsorption zone was moving through the bed was 0.80 cm/h. The percentage of the total column saturated at breakthrough was found to be 47.12%. The fixed bed column was designed by logit method [37,38]. The logit equation can be written as

$$\ln \left[\frac{C/C_0}{1 - C/C_0} \right] = -\frac{KNX}{V} + KC_0t \quad (20)$$

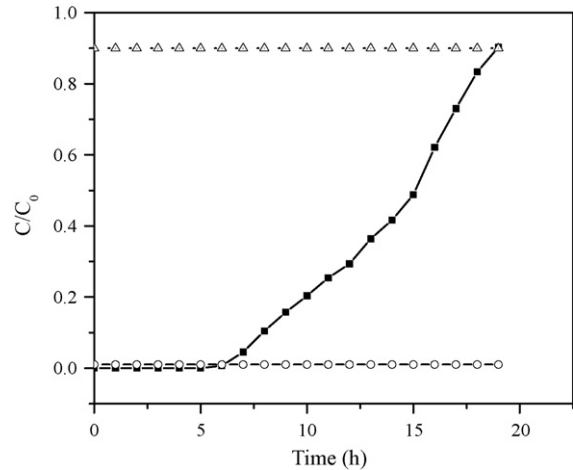


Fig. 12. Breakthrough curve for arsenic using laterite soil.

where C is the solute concentration at any time t , C_0 the initial solute concentration (0.33 ppm), V the approach velocity ($\sim 149 \text{ cm/h}$), X the bed depth (10 cm), K the adsorption rate constant ($l/(\text{mg h})$), and N is the adsorption capacity coefficient (mg/l). Rearranging Eq. (20) we get:

$$\ln \left[\frac{C}{C_0 - C} \right] = -\frac{KNX}{V} + KC_0t \quad (21)$$

Plot of $\ln[C/(C_0 - C)]$ versus t gives a straight line with slope KC_0 and intercept: KNX/V from which K and N could be calculated. Plot of $\ln[C/(C_0 - C)]$ versus t was shown in Fig. 13. The value of adsorption rate coefficient (K) and adsorption capacity coefficient (N) was obtained as $1.21 \text{ l}/(\text{mg h})$ and 69.22 mg/l . These values could be used for the design of adsorption column.

3.3. Effluent water quality parameters

The water quality parameters of the effluent water after column adsorption were determined. It was observed that the adsorbent could remove iron (final concentration 0.1 ppm) and hardness (final concentration 150 ppm) to a great extent.

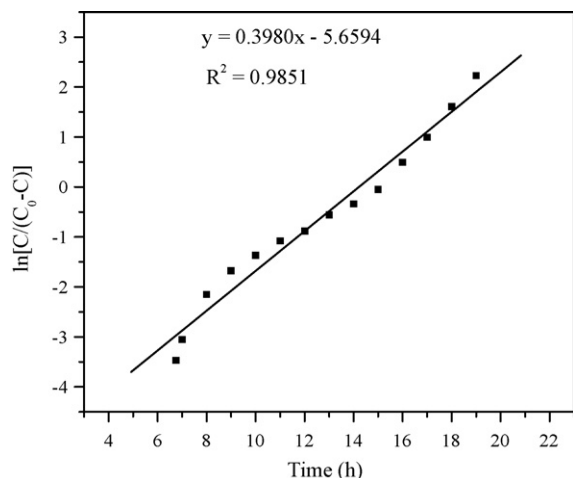


Fig. 13. Linearized form of logit model.

Tremendous decrease of conductivity (final conductivity 320 μS) in the effluent water was noticed indicating that there was significant removal of dissolved solids. Although the adsorbent material contains significant amounts of Cu and Al, there was no leaching of such ions in the effluent water observed. The pH of the effluent water remained almost same as in the influent water suggesting that no post treatment is necessary. In this context it is worth mentioning that in case of many adsorbent materials significant increase in the pH in the effluent water is noticed. All these suggested that laterite soil could be used as a potential adsorbent for adsorption and filtration columns.

3.4. Desorption study

The sorption process to be viable, the sorbent has to be amenable to efficient regeneration and reuse. The laterite soil was suitable for efficient regeneration by 1 M NaOH and it could subsequently be brought to service following a short rinse with distilled water. The regenerated adsorbent showed even better performance compared to the original soil. This is possibly due to the fact that on NaOH treatment the surface becomes fresh and the numbers of active sites are increased. Also the treatment causes the materials to become more porous. But keeping in mind the increase of cost of the material due to alkali treatment and the inconvenience to be faced by the common people during the treatment process (when the technology to be used for field applications), through the entire studies the laterite soil was used in its original natural state.

4. Conclusions

In the present study removal of arsenic from real-life groundwater was achieved using laterite soil as an adsorbent. The adsorbent is cost-effective and easy to separate from the effluent water. In batch study the optimum adsorbent dose and equilibrium time were found to be 20 g/l and 30 min, respectively. The adsorption was evaluated by the Langmuir, Freundlich and D–R isotherm models. The adsorption mechanism follows the pseudo-second-order reaction kinetics and the film diffusion is the rate-limiting step. In the column study the breakthrough time was found to be 6.75 h and the exhaust time was 19.0 h. The value of adsorption rate coefficient (K) and adsorption capacity coefficient (N) was obtained as 1.21 l/(mg h) and 69.22 mg/l, respectively. These values could be used for the design of adsorption column. The results obtained in this study will be useful for its further extension to field scale or for designing pilot plant as future studies. It is worth mentioning here that the laterite soil does not cause any increase in pH, or any increase in Fe(III)/Al(III)/Cu(II) concentration (due to leaching) in the effluent water. In addition, on column adsorption the effluent water quality is much improved.

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