



Sorption of As(V) from aqueous solution using acid modified carbon black

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ABSTRACT

The sorption performance of a modified carbon black was explored with respect to arsenic removal following batch equilibrium technique. Modification was accomplished by refluxing the commercial carbon black with an acid mixture comprising HNO₃ and H₂SO₄. Modification resulted in the substantial changes to the inherent properties like surface chemistry and morphology of the commercial carbon black to explore its potential as sorbent. The suspension pH as well as the point of zero charge (pH_{pzc}) of the material was found to be highly acidic. The material showed excellent sorption performance for the removal of arsenic from a synthetic aqueous solution. It removed ~93% arsenic from a 50 mg/L solution at equilibrium time. The modified carbon black is capable of removing arsenic in a relatively broad pH range of 3–6, invariably in the acidic region. Both pseudo-first-order and second-order kinetics were applied to search for the best fitted kinetic model to the sorption results. The sorption process is best described by the pseudo-second-order kinetic. It has also been found that intra-particle diffusion is the rate-controlling step for the initial phases of the reaction. Modelling of the equilibrium data with Freundlich and Langmuir isotherms revealed that the correlation coefficient is more satisfactory with the Langmuir model although Freundlich model predicted a good sorption process. The sorption performance has been found to be strongly dependent on the solution pH with a maximum display at pH of 5.0. The temperature has a positive effect on sorption increasing the extent of removal with temperature up to the optimum temperature. The sorption process has been found to be spontaneous and endothermic in nature, and proceeds with the increase in randomness at the solid–solution interface. The spent sorbent was desorbed with various acidic and basic extracting solutions with KOH demonstrating the best result (~85% desorption).

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1. Introduction

Arsenic contaminated drinking water is a major water born environmental problem. Consumption of arsenic containing water causes serious health-related problems because of its toxicity. The symptoms of chronic poisoning on human beings are numerous: skin cancer, liver, lung, kidney, and bladder cancers as well as conjunctivitis, melanosis, hyperkeratosis, and in severe cases gangrene in the limbs and malignant neoplasm [1,2]. Bangladesh is worst affected by this problem where concentration of arsenic has been reported to be nearly 180 times as high as the WHO limit of 0.01 mg/L [2,3]. The gravity of the problem is also alarming in China [4] and West Bengal, India [5]. Recently, arsenic pollution has been reported in Argentina, Mexico, Peru, Hungary, Taiwan, Greece, Canada, United States, Japan, Poland, Serbia, Montenegro and Chile [6–10].

Background arsenic concentrations in natural water are low [11], but elevated arsenic concentrations are common in groundwater as a result of natural conditions or anthropogenic impacts. Natural oxidation and/or reduction reactions involving arsenic-bearing rocks under favourable Eh and pH conditions may mobilize the arsenic and increase arsenic concentrations in groundwater [12]. Human activities that could increase arsenic concentrations in groundwaters and surface waters include oil and coal burning power plants, waste incineration, cement works, disinfectants, household waste disposal, glassware production, electronics industries, ore production and processing, metal treatment, galvanizing, ammunition factories, dyes and colours, wood preservatives, pesticides, pyrotechnics, drying agents for cotton, oil and solvent recycling and pharmaceutical works [13,14].

Arsenic has a rather complicated chemistry, because it can exist in several forms in the environment. Both organic and inorganic forms of arsenic are reported in natural waters, however the inorganic form dominates, and the amount of organic arsenic in drinking water sources is insignificant. Inorganic arsenic produces a variety of compounds because of its variable oxidation states (–3, 0, +3 and +5) [15]. The inorganic species, arsenate (As(V)) and arsenite

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(As(III)), are the arsenicals of concern in drinking water sources [16]. As(V) species are found in oxidizing environment, while As(III) are present in anoxic and reducing environments [17,18]. In ground water, the major species, As(V) exists as monovalent H_2AsO_4^- and divalent HAsO_4^{2-} anions resulting from the dissociation of arsenic acids (H_3AsO_4); while, As(III) species exists as uncharged arsenious acid (H_3AsO_3) [19,20].

Literature survey reveals that there are a good number of approaches for arsenic remediation from drinking water. Amongst the various methods like oxidation–reduction, precipitation, co-precipitation, sorption, electrolysis and cementation, solvent extraction, ion exchange, ion flotation, foam flotation and bioremediation [21–26] proposed to negotiate the problem of arsenic contamination in drinking water, sorption technique is, however, the most common and is considered to be an effective method. This method is simple and convenient, and also has the potential for regeneration and sludge-free operation. Sorbents of different types like biomaterials [27], metal oxide/hydroxide [28,29], zeolite [30], activated carbon [31], etc. have been used by workers to achieve the goal. The recent review on arsenic removal by Mohan and Pittman [32] gives a comprehensive idea about the different adsorptive processes investigated for arsenic remediation.

There are increasing interests on enhancing the effectiveness of sorbents by tailoring the specific properties of the sorbents to enable them to develop affinity for contaminants. Much work has focused on surface modification of the sorbents. This recent trend of using surface-modified sorbents is becoming a potential research field for the development of efficient and cost effective arsenic removal technique. Modified sorbents like iron oxide coated polymeric materials, iron oxide coated sand, lanthanum-impregnated silica gel, zirconia impregnated activated carbon, iron-containing granular activated carbon, polyaniline modified granular activated carbon, etc. have been reported [33–37]. It has been observed that significant amount of work is focused on carbonaceous materials particularly with activated carbon, but carbon black is scarcely used in sorption studies for the removal of contaminants from water/wastewaters. There is, however, no published report on the sorption of arsenic by using virgin or modified carbon black.

The virgin carbon black showed excellent sorption ability for the removal of As(V) from aqueous phase and the results are reported elsewhere [38]. Sorption performance of more than 90% was achieved which in fact instigated us to extent our work. The present work is an attempt to modify the virgin carbon black to tailor some of its properties particularly from sorbent perspective and to exploit in the sorption of arsenic. The principal objectives of the work include: (i) modification of the virgin carbon black by refluxing with a mixture of HNO_3 and H_2SO_4 , (ii) investigation of the influence of various physicochemical parameters controlling the sorption process, (iii) search for the best fitted kinetic model to understand the sorption mechanism, and (iv) modelling of sorption equilibrium using Freundlich and Langmuir isotherms with least-square regression.

2. Materials and methods

2.1. Materials

The sorbent for this study was prepared from a commercial carbon black (MA 100) obtained from Mitsubishi Chemicals, Japan. The material is of powder type with a particle size of 24 nm. There is no information available regarding the method and the type of precursor material used for the preparation of the carbon black. Modification of carbon black was accomplished using a mixture of HNO_3 and H_2SO_4 . Ionic strength of solutions was adjusted using

NaNO_3 . Adjustment of pH was done using HNO_3 and NaOH . Stock solution of arsenic was prepared from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$. All chemicals were of analytical grades and were purchased from Wako Chemicals, Japan. Deionized water was used in all experiments (pH, 6.75; specific conductivity, 0.30×10^{-4} S/m).

2.2. Sorbent modification

Modification of carbon black was done by refluxing about 10.0 g of the material with 250 mL of a mixture of 20% HNO_3 and 20% H_2SO_4 (equal volumes of each acid) at 110°C for 90 min. Prior to refluxing, N_2 was purged through the mixture for 10 min. The product was filtered after allowing the mixture to cool down to room temperature, washed with deionized water until the filtrate was free from nitrate or sulphate (verified by negative results of the corresponding qualitative tests), and the pH became neutral. Finally, the sample was dried in a vacuum oven at 80°C for 24 h.

2.3. Sorption experiments

Prior to experimentation, a stock solution of arsenic of desired strength was prepared by dissolving an appropriate amount of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in deionized water. Test solutions were prepared from the stock solution with appropriate dilution. The effect of contact time, solution pH, initial concentration of arsenic and temperature were studied. Each experiment was carried out by suspending 50 mg of sorbent in 50 mL of sorbate solution taken in Erlenmeyer flask under appropriate conditions set out for the experiment. The suspensions were equilibrated for 2 h in a shaker bath set at 200 rpm under laboratory temperature ($20 \pm 1^\circ\text{C}$). The ionic strength of the solution was adjusted to 0.1 M using NaNO_3 solution. The final volume of the solution was made up to 100 mL by adding deionized water. There is no control over pH of the solutions during experimentation. After the completion of experiments, the suspension was filtered, washed several times with deionized water and analysed for As(V) using an Inductively Coupled Plasma-Atomic Emission Spectroscopy (Model: ICPS-7500 Sequential Plasma Spectrophotometer, Shimadzu, Japan). Initially, samples were acidified with concentrated nitric acid and then filtered with a $0.45 \mu\text{m}$ Cellulose Acetate (hydrophilic) filter (Japan) before analysis. Solution pH was measured using a digital pH meter (Model: D-51, Horiba, Japan).

2.4. Retrospective theories of sorption

2.4.1. Sorption performance

The sorption performance is quantified in terms of metal uptake, q_e (mg/g). The corresponding material balance in the batch reactor can be expressed as

$$m(q_e - q_0) = V(C_0 - C_e) \quad (1)$$

or

$$q_e = (C_0 - C_e) \times V/m, \quad \text{when } q_0 = 0. \quad (2)$$

where q_0 and q_e are the metal uptakes at initial and equilibrium conditions, respectively by the sorbent (mg/g); C_0 , and C_e are the initial and equilibrium concentration of metal in bulk solution (mg/L); V is the volume of the aqueous phase (L) and m is the mass of the sorbent (g).

2.4.2. Sorption dynamics

The suspensions containing 50 mg of sorbent and 100 mg/L As(V) solution were shaken in different time intervals ranging from 5 to 200 min, filtered and metal were analysed in the filtrate. The

pH of the solutions was fixed at 3.0 just below the pH_{pzc} for multi-valent cation sorptions are often studied at a pH below the pH_{pzc} . The results were analysed using the following models in order to express the kinetics of the sorption process.

- (a) The linear form of the pseudo-first-order kinetic model proposed by Lagergren [39] can be expressed as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_t and q_e are the amounts of metal ion sorbed per unit mass (mg/g) at time, t (min) and at equilibrium time respectively, and k_1 is the specific sorption rate constant (min^{-1}). The plot of $\ln(q_e - q_t)$ versus t should result in a straight line. The rate constant can be calculated from the slope of the straight line.

- (b) The linear form of the pseudo-second-order rate expression [40] is given by

$$\frac{t}{q_t} = \frac{1}{k_2} q_e^2 + \frac{t}{q_e} \quad (4)$$

where k_2 is the pseudo-second-order rate constant. Other terms have their usual meanings. The plot of t/q_t versus t should yield a straight line which allows computation of k_2 . In Eq. (4), the expression $k_2 q_e^2$ in the intercept term describes the initial sorption rate, r (mg/g min) as $t \rightarrow 0$.

$$r = k_2 q_e^2 \quad (5)$$

- (c) Intra-particle diffusion is an important phenomenon for sorption processes in porous materials. The initial rate of intra-particle diffusion can be calculated using the following expression [41].

$$q_t = k_{\text{id}} t^{0.5} \quad (6)$$

where k_{id} is the intra-particle diffusion rate constant and the meanings of rest of the terms were already stated. This model predicts that the plot of q_t versus $t^{0.5}$ should be linear if intra-particle diffusion is involved in the sorption process. Intra-particle diffusion would be the rate-controlling step if the line passes through the origin.

2.4.3. Sorption modelling

The suspensions containing 50 mg of sorbent and 50 mL of As(V) solution of different initial concentrations (5–200 mg/L) were equilibrated for 2 h, filtered and metal were analysed in the filtrate. The pHs of this set of experiments were fixed at 3.0. The equilibrium concentrations of the sorbate in the liquid and solid phases were modelled using the well-known Freundlich and Langmuir isotherms [42,43].

- (a) The Freundlich isotherm in its linear form can be expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

where q_e (mg/g) and C_e (mg/L) are the equilibrium concentrations of As(V) in the solid and liquid phases, respectively. K_F and $1/n$ are characteristic constants related to the relative sorption capacity of the sorbent (mg/g) and the intensity of sorption, respectively. The logarithmic plot of q_e against C_e should result in a straight line that allows computations of $1/n$ and K_F from the slope and intercept, respectively.

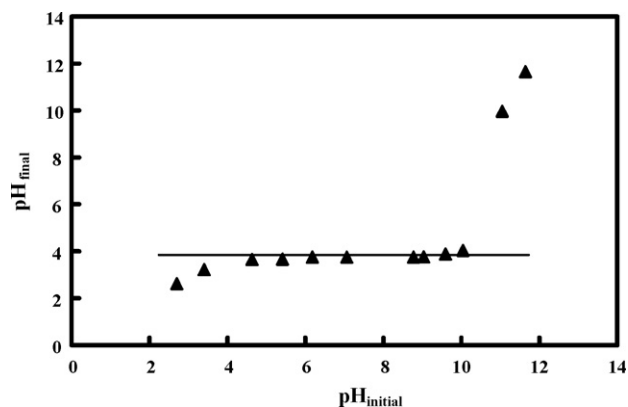


Fig. 1. Plot of pH_{final} against $\text{pH}_{\text{initial}}$ for the determination of pH_{pzc} of the modified carbon black. Sorbent: 50 mg; background electrolyte: 0.1 M NaNO_3 ; equilibration time: 6 h, and temperature: $20 \pm 1^\circ\text{C}$.

- (b) The linear form of the Langmuir isotherm can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (8)$$

where Q_m is the measure of monolayer sorption capacity (mg/g) and b is a constant related to the free energy or net enthalpy of sorption ($b \propto e^{-\Delta G/RT}$). The rest of the terms have their usual meanings as described above.

2.4.4. Thermodynamics of sorption

The thermodynamic parameters such as Gibbs free energy (ΔG°) can be obtained from the well-known Gibbs–Helmholtz relation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

where ΔH° and ΔS° are the enthalpy change and entropy change, respectively. The corresponding values of ΔH° and ΔS° can be estimated from the relationship between equilibrium constant (or distribution coefficient, K_d) and ΔH° defined by the Clausius–Clapeyron type of equation which in fact is the thermodynamic basis for predicting the change in equilibrium constant with temperature.

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where K_d is defined as

$$K_d = \frac{(C_o - C_e)}{C_e \times V/m} \quad (11)$$

where the symbols have their usual meanings. The plot between $\ln K_d$ and $1/T$ should be linear and the slope and intercept of the plot gives the values of ΔH° and ΔS° , respectively.

3. Results and discussion

The modified carbon black was characterized and compared with the virgin carbon black prior to sorption studies, and the results are reported elsewhere [44]. Briefly, acid treatment resulted in the changes of surface chemistry; textural properties and morphology as evidenced from the instrumental analysis. Compared to the virgin carbon black, the suspension pH (virgin: 6.5 and modified: 4.5) and pH_{pzc} (virgin: 6.4 and modified: 3.7) are highly acidic for the modified. Fig. 1 shows the representation for the determination of pH_{pzc} . The plateau corresponding to the plot of pH_{final} against $\text{pH}_{\text{initial}}$ gives the value of pH_{pzc} . The corresponding batch experiments were performed by suspending known amounts of

Table 1
Characteristics IR bands of the modified carbon black

IR band	Assignment	Position, cm^{-1}	
		Virgin	Modified
$\nu_{\text{O-H}}$ in-plane deformation	Hydroxyl	1460–1420	1460–1420
$\nu_{\text{C=C}}$ stretching	Aromatic ring structures	1575–1550	1575–1550
$\nu_{\text{C=O}}$ stretching	Ketones, aldehydes, lactones or carboxyl	1730–1670	1730–1670
$\nu_{\text{-NO}_2}$ symmetric stretching	Nitro	–	1539
$\nu_{\text{-SO}_2}$ symmetric stretching	Sulphonic acid ($-\text{SO}_2\text{OH}$)	–	802
$\nu_{\text{-SO}_2}$ asymmetric stretching	Sulphonic acid ($-\text{SO}_2\text{OH}$)	–	1260

For comparison purpose IR bands of virgin carbon black included.

sample (50 mg) in 50 mL 0.1 M NaNO_3 solution (background electrolyte). The interaction amongst the ions in a multi-ionic system is highly influenced by the ionic composition of the solution, and therefore, NaNO_3 was used with the objective to maintain the ionic strength of the systems constant during experimentation. Initial pH of the solutions was adjusted and the suspensions were equilibrated for 6 h at 200 rpm in a shaker bath at laboratory temperature ($20 \pm 1^\circ\text{C}$). Finally, the suspensions were filtered and the pH of the filtrates was measured. Highly acidic nature of both suspension pH and pH_{pzc} is due to the creation of surface acidic functional groups during modification. Presence of oxygenated functional groups like $-\text{COOH}$ and $-\text{SO}_2\text{OH}$ were detected in the modified carbon black through FTIR study. For clarity, some of the important bands identified in the spectrum of the modified carbon black are presented in Table 1. SEM analysis revealed agglomeration as well as creation of extensive surface roughness. This resulted in the increase of active surface area (S_{BET}) of the material (virgin: $59.4 \text{ m}^2/\text{g}$ and modified: $61.4 \text{ m}^2/\text{g}$). Like the parent material, the modified carbon black is exclusively mesoporous with pore size ranging from 15 to 65 nm. These changes are expected to brought about significant sorption performance of the material and deserve exploration. Pentavalent arsenic was removed from a synthetic aqueous solution using the modified carbon black and the effect of various physicochemical parameters influencing sorption was investigated.

3.1. Effect of contact time and sorption dynamics

The results of the effect of equilibrium time on the sorption of As(V) by modified carbon black is shown in Fig. 2. It is evident that the removal of As(V) takes place in two distinct steps: a relatively fast phase continuing up to 75 min followed by a slow progress to the state of equilibrium. The necessary time to reach the equilibrium is about 90 min. This infers fast sorption kinetics and bulk of

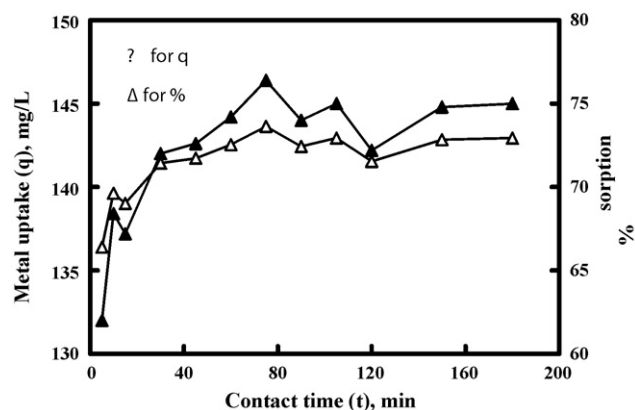


Fig. 2. Effect of contact time on metal uptake and % sorption by the modified carbon black. Concentration of As(V): 100 mg/L; sorbent: 50 mg; background electrolyte: 0.1 M NaNO_3 ; solution pH: 3.0, and temperature: $20 \pm 1^\circ\text{C}$.

the solute is being removed ($\sim 70\%$) within an hour. The high initial uptake rate is due to the availability of a large number of sorption sites at the onset of the process. The sticking probability is also high on the bare surface accounting high sorption rate. Further, the material is exclusively mesoporous and therefore, the diffusion of solute into the pores appears to be easier. Faster solute removal as well as low equilibration time attributes highly favourable sorptive interactions. Similar kind of behaviour was also observed with the virgin carbon black [38]. For subsequent experiments, an equilibration time of 2 h was chosen for the sake of convenience.

The application of the different kinetic models unveiled some interesting features regarding the mechanism and rate-controlling step in the overall sorption process. In the first instance, the Lagergren pseudo-first-order kinetic model was applied (figure omitted for the sake of brevity). Though the plot shows good linearity with a correlation coefficient of 0.9141 yet the equilibrium metal uptake (q_e) obtained from the kinetic plot deviated much from the experimental value (-13.2%). Thus the model is insufficient to explain the kinetics of the sorption process and can be rejected based on this solid ground. This enables us to apply the pseudo-second-order kinetic model to verify the kinetics of sorptive interactions. The plot of t/q_t against t showed better linearity with a correlation coefficient of 0.9998 (figure omitted for the sake of brevity). The initial sorption rate (r), the equilibrium sorption capacity (q_e) and the rate constant (k_2) were calculated from the slope and intercept of the straight line and are reported in Table 2. The difference between the equilibrium metal uptakes (q_e) obtained from the kinetic plot and the experimental value is quite small ($+1.8\%$). Nevertheless, the difference persists even though it is small. This may be due to the actual process that cannot be described by a simple first-order or second-order kinetics. However, a correlation coefficient closer to unity for second-order model justifies that the sorption kinetics could well be explained and approximated more favourably by the pseudo-second-order kinetics.

The sorption of a solute from solution by porous sorbents is essentially associated with three consecutive mass transport steps.

Table 2
Kinetic parameters for arsenic sorption onto modified carbon black

Model/parameters	Value
<i>Pseudo-first-order model</i>	
k_1, min^{-1}	4.9×10^{-2}
$t_{1/2}, \text{min}$	14.1
R^2	0.9141
q_e (experimental), mg/g	144.2
q_e (kinetic plot), mg/g	125.1
<i>Pseudo-second-order model</i>	
$k_2, \text{g mg}^{-1} \text{min}^{-1}$	11.9×10^{-2}
R^2	0.9998
q_e (experimental), mg/g	144.2
q_e (kinetic plot), mg/g	146.8
<i>Intra-particle diffusion model</i>	
$k_{\text{id}}, \text{mg g}^{-1} \text{min}^{-0.5}$	24.7

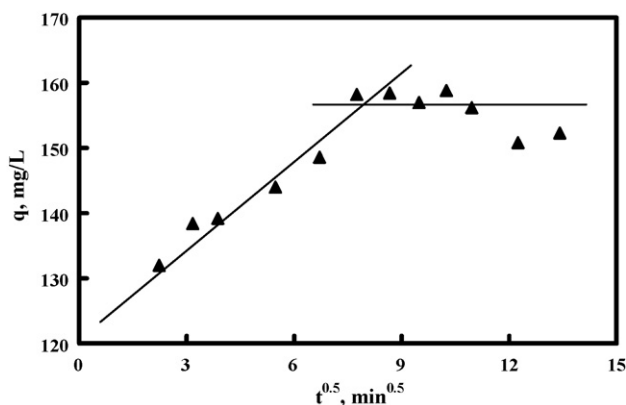


Fig. 3. Weber and Morris intra-particle diffusion kinetic plot of q_t versus $t^{0.5}$ for the sorption of As(V) by modified carbon black.

(i) Film diffusion: involves the transport of the sorbate to the external surface of the sorbent, (ii) Particle diffusion: involves the preponderance transport of the sorbate within the pores of the sorbent with a small amount of sorption on the external surface of the sorbent, and (iii) Sorption: involves the adherence of the sorbate on the exterior surface of the sorbent. Bulk transport of solute in the solution phase, usually is rapid because of mixing and convective flow. Film transport results in the diffusion of the solute through a hypothetical “film” or hydrodynamic boundary layer. Intra-particle diffusion or pore diffusion involves the transport of the sorbate from the particle surface into the interior sites by diffusion within the pore-filled liquid and migration along the solid surface of the pore. Film and pore transports are the two major factors controlling rates of sorption from solution by porous sorbents. These clearly explain the need to identify the rate-limiting step that governs the overall rate of the sorption process.

The results were further subjected to analysis by the intra-particle diffusion model devised by Weber and Moris [41]. A functional relationship common to most treatments of intra-particle diffusion is that uptake varies almost proportionately with the half power of time $t^{0.5}$, rather than t ; a nearly linear variation in the quantity sorbed with $t^{0.5}$ is predicted for a large initial fraction of reactions controlled by rates of intra-particle diffusion. Good linearization of the data is observed for the initial phase of the reaction in accordance with expected behaviour if intra-particle diffusion is the rate-limiting step [41]. Further, if the rate-limiting step is intra-particle diffusion, a plot of solute sorbed against the square root of the contact time should yield a straight line passing through the origin [45]. The initial rate of intra-particle diffusion (k_{id}) can be calculated using Eq. (6). The model states that a plot of q_t versus $t^{0.5}$ should be linear if intra-particle diffusion is involved in the overall sorption process. The plot of q_t against $t^{0.5}$ in Fig. 3 shows that the relationship is not linear for the entire range of reaction time. The line is not passing through the origin, and consequently, intra-particle diffusion was not the rate-limiting step in the sorption process. The plot shows two straight parts. This attributes operation of two types of mechanisms in the sorption process and could be due to the varying extent of sorption in the initial and final stages of the experiment. The first linear part represents initial rapid uptake due to film diffusion and consequent external surface coverage by the sorbate. The second linear part explains the transportation of sorbate into the sorbent particles. It is clear from Fig. 3 that the relationship yield a straight line through the origin for the beginning part, and this was more likely to occur at lower initial As(V) concentrations. It may be concluded that the rate-limiting step is intra-particle diffusion in the initial period of the reaction.

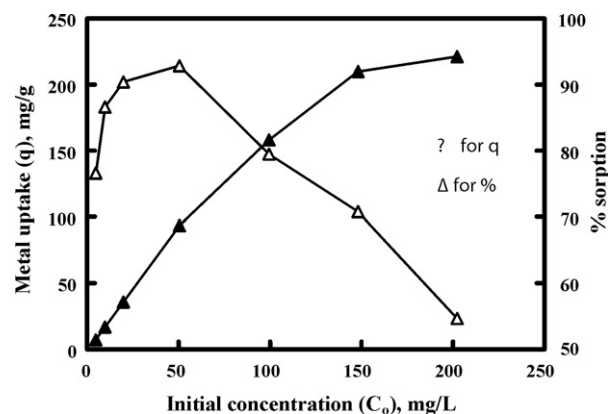


Fig. 4. Effect of initial As(V) concentration on metal uptake and % sorption by the modified carbon black. Concentration of As(V): 5–200 mg/L; sorbent: 50 mg; background electrolyte: 0.1 M NaNO₃; solution pH: 5.0; equilibration time: 2 h, and temperature: 20 ± 1 °C.

3.2. Effect of initial arsenic concentration and sorption modelling

The plot of As(V) sorbed by the modified carbon black against metal concentrations in the equilibrated solutions is presented in Fig. 4. This set of experiments was performed at 20 ± 1 °C by varying the metal concentration from 5 to 200 mg/L while keeping other experimental conditions constant. There is continuous increase of metal uptake with the increase of As(V) concentration, until the equilibrium is reached. With the increase of the concentration of As(V) in solution, the availability of arsenate ions also increases at the solid–solution interface resulting in the increase of sorption performance. However, the saturated point of sorption is reached when the limited active surface sites on the sorbents are covered fully by the sorbate. Further the heterogeneous nature of the sorbents with regards to the distribution of the binding sites predicts that all the active sites are not equally effective. The sites which have higher affinity towards As(V) might have contributed to sorption.

The equilibrium data have been correlated with the Freundlich and Langmuir isotherms over the entire concentration range. The Freundlich plot has a regression coefficient of 0.9568 indicating a near-perfect linear relationship between $\log q_e$ and $\log C_e$ (figure omitted for the sake of brevity). The constants K_F and $1/n$ computed from the linear plot are presented in Table 3. The numerical value of $1/n < 1$ indicates an unfavourable sorption of As(V) onto modified carbon black. This is likely to be the case at relatively higher metal concentration where the electronic and coulombic repulsive forces amongst As(V) species dominates over the attractive forces of sorption. This phenomenon could be well explained with the results of Fig. 4. After a certain concentration, though there is continuous increase of metal uptake yet % sorption decreases. The increase in the values of metal uptake is due to the mathematical basis of its computation (Eq. (2)). However, a clear understanding about the actual process involved could be obtained from % sorp-

Table 3
Isotherm parameters for arsenic sorption onto modified carbon black

Isotherm/parameters	Value
<i>Freundlich isotherm</i>	
K_F , mg g ⁻¹	24.4
$1/n$	0.6801
R^2	0.9568
<i>Langmuir isotherm</i>	
Q_m , mg g ⁻¹	46.3
b , L mg ⁻¹	0.0692
R^2	0.9929

tion. Decrease in % sorption at higher metal concentrations explains the unfavourable nature of sorption influenced by repulsive forces. However, it is a good sorption process at lower concentrations because values of n between 2 and 10 can be recognized as good sorption [46]. The K_F value of the sorption process shows easy uptake of As(V) by the sorbent with high sorptive capacity. It is difficult to predict surface saturation based on the K_F value for the mathematical basis of the model refers to extended surface coverage leading to multilayer sorption.

The Langmuir model parameters estimated from the slope and intercept of the linear plot using a statistical fit are given in Table 3 (figure omitted for the sake of brevity). The Langmuir model effectively describes the sorption data with a correlation coefficient of 0.9929. Thus the isotherm follows the sorption process in the entire concentration range studied. Comparatively, the correlation coefficient is more satisfactory for the Langmuir isotherm and therefore, equilibrium sorption of As(V) onto modified carbon black is best described by the Langmuir model. The sorption capacity (monolayer coverage, Q_m) is lower (Table 3) than that determined from the pseudo-second-order kinetic model (Table 2). This can be attributed to the difference in solution conditions, viz. sorbate to sorbent ratio and initial concentration of As(V) between the sorption isotherm and kinetic experiments.

The dimensional constant, called separation factor (R_L) proposed by Hall et al. [47] can be used to describe the essential characteristics of a Langmuir isotherm.

$$R_L = \frac{1}{(1 + bC_0)} \quad (12)$$

where the terms have their meanings as stated above. In fact, the separation factor is a measure of the sorbent capacity used. Its value decreases with increasing 'b' as well as initial concentration. R_L values can be related to the equilibrium isotherm as follows:

$R_L > 1$ unfavourable

$R_L = 1$ linear

$0 < R_L < 1$ favourable

$R_L > 0$ irreversible

The values were calculated for the entire concentration range studied and the results are found to lie in between 0 and 1 demonstrating a favourable sorption process.

3.3. Effect of solution pH and mechanism of sorption

The sorption performance of carbonaceous materials is highly influenced by the solution pH due to the presence of significant amount of surface acidic functional groups. Sorption experiments were performed by equilibrating suspensions containing 50 mg of the modified carbon black in 50 mL of 100 mg/L strength As(V) solution at a fixed initial pH with NaNO₃ as the background electrolyte in batch mode. Initial pHs were restricted in the range of 2.0–11.0. The results thus obtained are presented in Fig. 5. It is evident that As(V) sorption is strongly pH dependent. The As(V) sorption increased sharply when the solution pH was changed from 3 to 4. The maximum metal uptake (~84%) was achieved at an initial pH of 5.0, even though the sorbent exhibited superior sorption performances in a wide pH range (3–6). Like the parent carbon black [38], it also exhibited better sorption performances in the acidic region. This could be due to the presence of significant amount of carboxylic and sulphonic acid groups created by the modification process. The soft-soft interaction between As(V) and sulphur donor ligands is highly favoured [19] and might have facilitated the sorption process.

It was also observed that sorption is accompanied with the changes in the pH of the medium as is evident from the results of

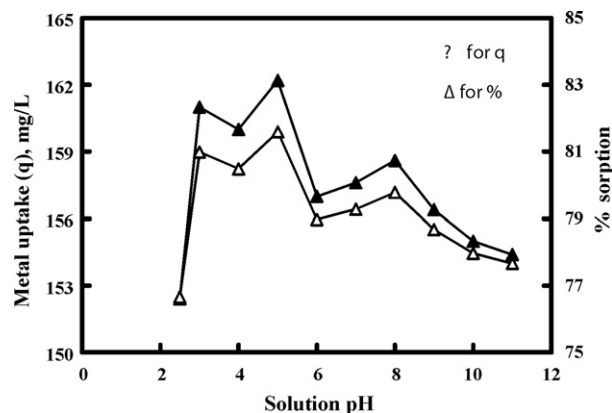


Fig. 5. Effect of initial solution pH on metal uptake and % sorption by the modified carbon black. Concentration of As(V): 100 mg/L; sorbent: 50 mg; background electrolyte: 0.1 M NaNO₃; equilibration time: 2 h, and temperature: 20 ± 1 °C.

Fig. 6. In the lower pH range of 2–4, the pH of the solution slightly shifted towards higher pH (i.e. basic). The pH shifts are on either side of the scale for the range of 5–7. Above pH 7, the shifts are towards the acidic region. This slight shift in pH may be attributed to the sorption reactions of As(V) with the concomitant release of OH groups from sorbent.

The pH dependence of metal sorption is influenced by two factors: (i) distribution of metal ions in the solution phase, and (ii) overall charge of the sorbent. Arsenic (V) exists in the form of H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻ and AsO₄³⁻ oxyanions depending upon the solution pH. The % distribution of various As(V) species against solution pH is shown in Fig. 7. The distribution profile was constructed as a function of solution pH based on the following three equilibrium and their respective stability constants.

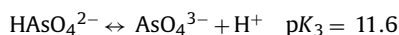
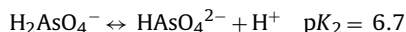
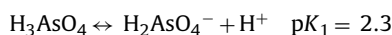


Fig. 7 indicates that oxyanions are the major species in a broad pH range. The negatively charged H₂AsO₄⁻ has its dominant presence in the pH range of 2–7, where maximum As(V) removal was observed is primarily responsible for sorption. Further, the surface charge of carbon-based sorbents is also highly influenced by the

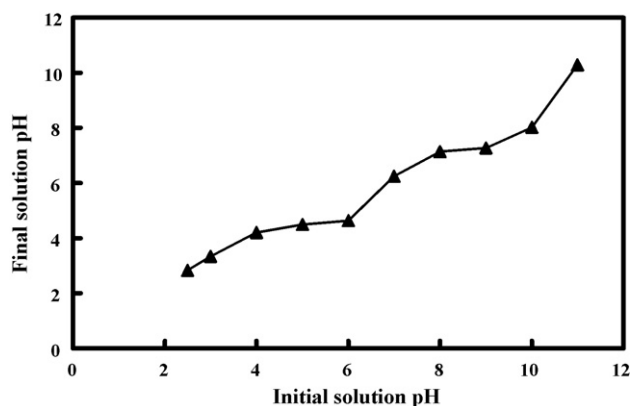


Fig. 6. Plot of final solution pH (pH_{final}) against initial solution pH ($pH_{initial}$) displaying the change of pH during sorption. Concentration of As(V): 100 mg/L; sorbent: 50 mg; background electrolyte: 0.1 M NaNO₃; equilibration time: 2 h, and temperature: 20 ± 1 °C.

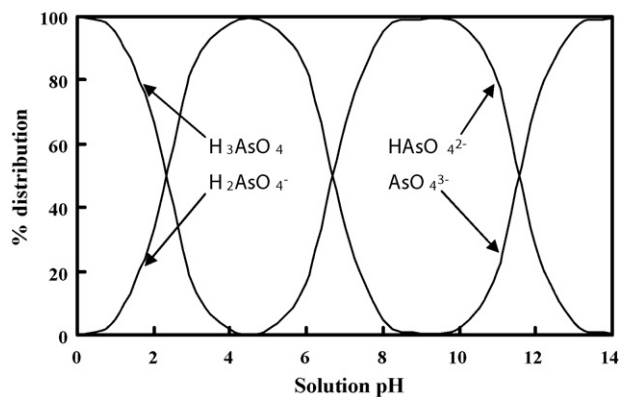


Fig. 7. Distribution (%) of various As(V) species as a function of solution pH.

solution pH. The pH at which the charge of the solid surface is zero is referred to as the zero point of charge (pH_{zpc}). The surface charge of the sorbent is positive below pH_{zpc} while it is negative above pH_{zpc} . A pH_{zpc} of 3.7 for the modified carbon black and the maximum sorption pH range of 3–6 attributes interaction of negatively charged As(V) species particularly H_2AsO_4^- with surface active groups of the carbon black. The modified carbon black contains significant amount of carboxyl and sulphonic acid groups as evidenced by IR spectra are responsible for the sorption of As(V) ions. Due to the presence of acidic moieties in the modified carbon, complexation with H_2AsO_4^- , HAsO_4^{2-} through OH ligands is favoured thereby facilitating As(V) removal. This might have resulted in the increase of removal performance in the pH range of 3–6 with the recording of maximum removal at pH 5.0. However, there is sharp decrease in the sorption performance below pH 3 and could be due to extensive protonation on the surface of carbon black. H^+ ions are abundant at lower pH and therefore, compete favourably to the carbon black surface in comparison to other ions. Further, it is clear from the percent distribution of arsenic species in aqueous media that neutral H_3AsO_4 is dominant at low pH which is not in favour of complexion.

3.4. Effect of temperature and sorption thermodynamics

The effect of temperature on sorption performance of As(V) onto the modified carbon black was investigated in the temperature range of 27–70 °C, and the results are depicted in Fig. 8. It shows that there is continuous increase in sorption with the concomitant increase of temperature. However, there is an optimum temper-

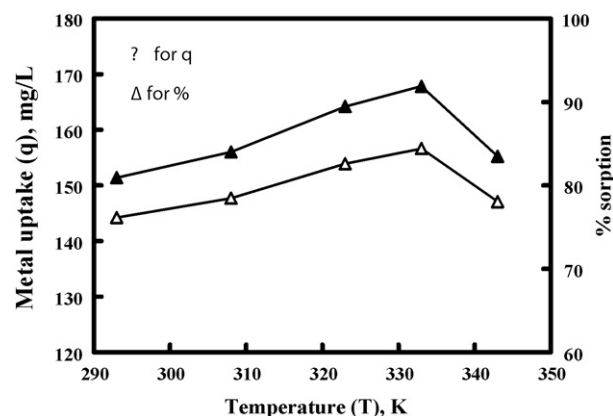


Fig. 8. Effect of temperature on metal uptake and % sorption by the modified carbon black. Concentration of As(V): 100 mg/L; sorbent: 50 mg; background electrolyte: 0.1 M NaNO_3 ; solution pH: 5.0, and equilibration time: 2 h.

Table 4
Thermodynamic parameters for arsenic sorption onto modified carbon black

Temperature/K	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta G^\circ/\text{kJ mol}^{-1}$
293	7.8	42.1	-4.6
308			-5.2
323			-5.8
333			-6.2
343			-6.7

ature above which sorption performance decreases. The increase in the level of sorption with temperature could be due to increase in the activity of the sorption sites on the carbon black as well as enlargement of the pores [48].

The thermodynamic quantities ΔH° , ΔS° and ΔG° of As(V) sorption were calculated from the temperature dependence K_d values at equilibration times. The plot of $\log K_d$ versus $1/T$ gave a linear variation showing good relationship between distribution coefficient and temperature (figure omitted for the sake of brevity). Values of ΔH° and ΔS° were calculated from the slope and intercept, respectively of the plot using a linear fit to the data, and are presented in Table 4 along with the values of ΔG° estimated using Eq. (9). The positive value of ΔH° reveals that the process is endothermic in nature, i.e., sorption is accompanied with the absorption of heat. The value of ΔS° has been found to be positive. It infers increase of randomness at solid–solution interface during the fixation of As(V) species on the active sites of the sorbent. Moreover, positive value of ΔS° reflects affinity of the sorbent for the arsenic species. The spontaneous nature of the sorption process is evident from the negative values of ΔG° . The decrease in ΔG° value with increasing temperature reveal that sorption of As(V) onto modified carbon black becomes more favourable at higher temperatures.

3.5. Effect of eluents on desorption performance

From industrial and technological point of view, it is desirable to recover the sorbed material along with the sorbent in wastewater treatment processes. The reversibility of arsenic sorption onto modified carbon black was studied by desorbing spent sorbent using acidic (HCl and HNO_3) and basic (NaOH and KOH) extracting solutions. Spent sorbents for this study were prepared by equilibrating 1 g of the sorbent with 200 mL of 200 mg/L As(V) solution for 2 h at 200 rpm and 20 ± 1 °C in an isothermal shaker bath. In each desorption experiment, 50 mg of the spent sorbent was treated with 50 mL of 1 M desorption agent, allowed to equilibrate for the same equilibration time applied in sorption (2 h), filtered and finally As(V) content in the filtrate was determined. The results are presented in Fig. 9. It is clear that the desorption performance depends

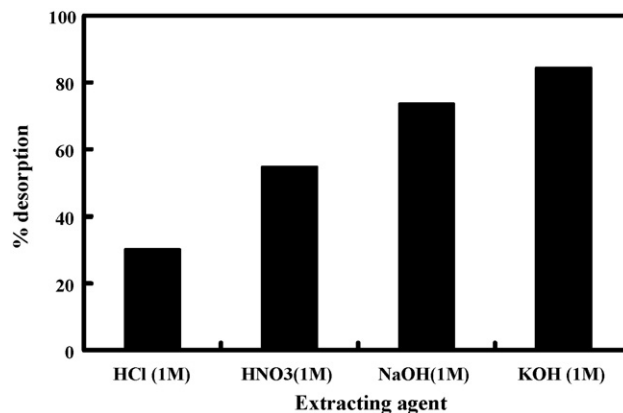


Fig. 9. Histograms showing the % desorption of As(V) using various leaching agents.

upon the nature of the solution. Both the two basic eluents showed superior desorption efficiency typically 30–50% higher desorption was achieved. The virgin carbon black also behaved in a similar manner [38]. Being reverse to the sorption process, the results of this desorption study are obvious. There are reports of using various strong acidic or basic solutions to achieve arsenic elution [49]. Similar kind of results were also reported by Amin et al. [49] in their work on the removal of As(III) and As(V) using rice husk, but the desorption performances achieved in this investigation is far better.

4. Conclusions

The sorption performance a modified carbon black for the removal of As(V) was evaluated. Modification was carried out by refluxing a commercial grade carbon black with a mixture of nitric and sulphuric acid. Some of the fundamental properties of the modified carbon black were determined from sorbent perspective. The suspension pH and pH_{pZC} were found to decrease substantially which demonstrates the creation of surface acidic functional groups during modification. This was conformed by the FTIR analysis. The sorption performance of the material was evaluated following batch equilibrium technique and the effects of various physico-chemical parameters controlling the rate of sorption were studied. The rate of sorption was very fast and equilibrium is reached within less than 2 h. The sorption process followed a pseudo-second-order kinetic with intra-particle diffusion controlling the rate in the initial period of the reaction.

The equilibrium sorption data were modelled using Freundlich and Langmuir isotherms. Freundlich model revealed that arsenic removal is a good sorption process. However, a comparison of the correlation coefficients demonstrates that the sorption process is best described by the Langmuir model. The dimensional separation factor used to predict the essential characteristics of Langmuir isotherm indicated favourable sorption in the entire concentration range.

The sorption performance has been found to be strongly dependent on the solution pH. The sorbent exhibited maximum sorption performance at a solution pH of 5.0 though it can effectively remove arsenic in a broader pH range. Arsenic speciation in water at various pH demonstrates that $H_2AsO_4^-$ is the dominant species in the pH range of 2–7, the range where the material exhibited higher sorption performances. This demonstrates that $H_2AsO_4^-$ is primarily responsible for arsenic removal.

Temperature dependence of sorption reveals the increase in sorption performance of the sorbent with temperature. The sorption process has been found to be spontaneous in nature and is accompanied with the absorption of heat. The increase in randomness at the solid–solution interface attributes the affinity of the carbon black sorbent for the arsenic species.

Desorption of arsenic from the spent sorbent has been found to depend upon the nature of the extracting solution. The desorption performance of the basic eluents were 30–50% more compared to the acidic solutions.

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