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Adsorptive Removal of Arsenite as (III) and Arsenate as (V) Heavy Metals from Waste Water using *Nigella sativa* L.

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Abstract: This study was focused on *Nigella sativa* Linn. as an alternative absorbent in order to remove As (III) and arsenate As (V) from synthetic waste water. As such, *Nigella sativa* L. was collected from Burydah A-Qassim. Batch experiments were conducted to determine the adsorptive efficiency of *Nigella sativa* L. to remove As (III) and arsenate As (V) from waste water. The preliminary experiments were revealed that alkaline solutions (pH>9) without *Nigella sativa* L. caused homogeneous oxidation of As (III) to As (V) so the adsorption process was investigated at pH range 2-8. The batch experiments were revealed that adsorption of As ion on *Nigella sativa* L. was maximal at low pH (at a 3.0) value. The adsorption studies revealed that the ongoing adsorption validates Langmuir adsorption isotherms at temperatures 25, 35 and 45°C. The adsorption isotherm data was also employed to calculate the thermodynamic parameter of Gibb's free energy which gives a negative value for the adsorption of As ion on *Nigella sativa* L. The negative values of free energy indicate the feasibility and spontaneous nature of the adsorption process. From these results, it can be concluded that the *Nigella sativa* L. could be a good adsorbent for the removal of cationic metals coming from waste water.

Key words: Adsorption, batch technique, heavy metals, langmuir adsorption, *Nigella sativa* Linn.

INTRODUCTION

Arsenic is a toxic trace element for animals including humans (Ahamed *et al*., 2006). Mineral dissolution, use of arsenical pesticides, disposal of fly ash, mine drainage and geothermal discharge elevate concentrations of in soils and waters (Smedley and Kinniburgh, 2005). Agricultural drainage waters from some soils especially in arid regions are elevated in As concentration. At natural pH arsenite exists in solution as H_3AsO_3 and $H_2AsO^{-}_3$, since the pK_a values for arsenious acid are high, $pK^1_a = 9.2$ and $pK^2_a = 12.7$. Arsenate is present as $H_2AsO_4^{-}$ and $HasO_4^{-2}$, since the pK_a values for arsenic acid are $pK^1_a = 2.3$, $pK^2_a = 6.8$ and $pK^3_a = 11.6$ (Masscheleyn *et al*., 1991). Because the kinetics of As redox transformations is relatively slow, both oxidation states are often found in soils regardless of the redox conditions (Masscheleyn *et al*., 1991). Adsorption studies of arsenite and arsenate have used a wide range of adsorbents including oxides, clay minerals, pretreated waste tea, fungal biomass, food by product as orange waste and mesoporous carbon Jang *et al*. (2006), Murugesan (2006), Ghimire *et al*. (2003) and Zhimang and Baolin (2007). Inorganic constituents of soils that adsorb significant amonnts of As are Al and Fe oxides, clay minerals and carbonates. Arsenate adsorption on iron-treated activated carbon, zeolites and bauxite (Payne and Abdel-Fattah, 2005) and (Bhakat *et al*., 2007) increased at low pH, exhibited maxima in the pH range 3 to 7 and decreased at high pH. Recently, it has been recognized that As (III) is more prevalent in groundwater than was

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earlierly understood (Korte and Fernando, 1991) which is of concern because it is more toxic than As (V) (Knowles and Benson, 1983). In addition, As (III) is a neutral, uncharged molecule (H_3AsO_3, pKa 9.2) (Korte and Fernando, 1991) at the pH of most natural waters. *Nigella sativa* L. is an indigenous herbaceous plant that is more commouly known as the feunel flower plant and belongs to the Buttercup or Ranunculaceae family. This plant which grows to a maximum height of about 60 cm, has finely divided foliage and blue flowers from which are produced small caraway-type black seeds. The plant is also known by other name e.g., black cumin (English), block caraway seeds (USA) and habba-tu sawda (Arabic). The total fixed oil (fatty acids) content of *Nigella sativa* L. has been determined to be >30% (Rathee *et al*., 1982). Qualitative chemical analysis of the *Nigella sativa* L. by capillary GC-MS technique has enabled the identification of 67 compounds which when classified into various functioual groups corresponded to the following data: monoterpines (46%); carbonyl compounds (25%); phenols (1.7); alcohols (0.9%) and esters (16%) (Aboutable *et al*., 1986); (Cheikh *et al*., 2007). The aromatic volatile oil content of *Nigella sativa* L. has been found to be 0.4-0.5% w/w. (Sejal, 2003). *Nigella sativa* seed oil has been examined to contain the following fatty acid composition of the triglyceride portion: linoleic (59.6%), olieic (23.8%), palmitic (12.4%) and stearic (<1%). The major triacylglycerols found were trilinoleoly (24.6%), oleoyldilinoleoyl (19.6%), palmitoyldilinoleoyl (17.5%), palmitoyloleoyllinoleoyl (12.9%) and dioleoyllinoleoyl (9.6%) (Abdel-Ghany *et al*., 1998). Total lipid content of the oil has been reported to be 31.8% in which neutral lipids predominate. The minor lipids consisted of glycolipids (Abdel-Ghany *et al*., 1998). This study had the following objectives: (1) to determine arsenate and arsenite adsorption on *Nigella sativa* L. as a function of solution pH and different temperature and (2) to evaluate the ability of the constant capacitance model to fit arsenite and arsenate adsorption on the negative sites on *Nigella sativa* L. in single-ion systems.

MATERIAL AND METHODS

Chemicals and Adsorbent

Nigella sativa L. was collected from Burydah A-Qassim Saudi. The cleaning of *Nigella sativa* L. was made using distilled water before using them as adsorbent. All other reagents used were of A.R. grade. For all experimental purposes 0.001 mg L^{-1} aqueous stock solution of the arsenite and arsenate were prepared. *Nigella sativa* L. composed of various organic compounds that have different functional group of NH_2 of monoterpines, CO of esters, OH of phenols and alcohols (Basha *et al*., 1995; Atta-ur-Rahman *et al*., 1995).

Preparation and Activation of Adsorbent

Nigella sativa L. was first agitated thoroughly in the distilled water bath and then rinsed several times to remove dirt from it. This was then kept in an oven at 100°C for 12 h for the removal of moisture and fiually stored in vacuum desiccators.

Arsenic Determination

Arsenic was determined in all extracts by High-Performance Liquid Chromatography-Hydride Generation Atomic Absorption Spectrophotometry (HPLC-HGAAS) as outlined in detail in a previous paper (Manning and Martens, 1997). Most samples were also run by continuous flow-through HGAAS without HPLC separation for comparison and excellent agreement between the two techniques was found for both single ion and mixed ion solutions. Arsenic single ion of (As (III), As (V) working standards (0.001-0.0001 mg L^{-1} As) were prepared fresh daily in either 0.01 mg L^{-1} NaCl or 0.001 M PO4 matrix for HPLC-HGAAS analysis.

As(III) and As(V) Adsorption Experiments

Stock solutions of 0.001 mg L^{-1} As (III) or As (V) in deionized (DI) water were made from $NaAsO_2$ and $Na_2HAsO_4,7H_2O$, respectively. All adsorption measurements carried out through batch technique at different temperatures of 25, 35 and 45°C. Batch adsorption of As (III) and As (V) was examined by shaking *Nigella sativa* L. in 100 mL polycarbonate centrifuge tubes containing 0.1 g of *Nigella sativa* L. in 50 mL of 0.0001 mg L^{-1} As (III) or As (V) for 24 h. Initial pH values before adjustment were approximately using 1 N HCl or NaOH additions that changed the total volume by 2%. After the 24 h reaction period to achieve equilibrium. However, in case of kinetics measurements the flask was shacked only for the desired time period. The tubes were centrifuged at 1000 run per min and pH was determined directly in supernatants with a pH electrode followed by filtering with 0.1 µm Whatman cellulose nitrate membranes. Arsenic speciation was then determined on these solutions. The fractional As (III) and As (V) adsorption was calculated as:

$$q = (C_0 - C) \times V/m \tag{1}$$

where, C_0 is the initial concentration of metal (mg L^{-1}), C is the equilibrium concentration of As in solution (mg L^{-1}), m is the mass of the adsorbent (g) and V is the volume of solution.

Surface Reactions

The Constant Capacitance Model (CCM) was used to describe arsenite and arsenate adsorption behavior on *Nigella sativa* L. as a function of solution pH. In the Constant Capacitance Model (CCM), the protonation and dissociation reactions for the surface functional group, Ar-OH, Ar-O and Ar-N (where Ar-OH, Ar-O and Ar-N represents a reactive surface hydroxyl, carbonyl and amino group that bound to a metal ion, (Ar is aromatic ring attached the hydroxyl group). The reactions of As (III) with As (V) on *Nigella sativa* L. surface in constant capacitance model can be represented by the following equations:

Surface Acid-Base Reactions

$$ArOH + H^+ \leftrightarrow SOH_2^+$$
$$ArOH \leftrightarrow ArO^- + H^+$$

Mononuclear As(V) Adsorption

$$ArOH + H_3AsO_4 \leftrightarrow ArH_2AsO_4 + H_2O$$
$$ArOH + H_3AsO_4 \leftrightarrow ArHA_sO_4^- + H_2O + H^+$$
$$ArOH + H_3AsO_4 \leftrightarrow ArAsO_4^{-2} + H_2O + 2H^+$$

Mononuclear As (III) Adsorption

$$ArOH + H_3AsO_3 \leftrightarrow ArH_2AsO_3 + H_2O$$
$$ArOH + H_3AsO_3 \leftrightarrow ArHAsO_3^- + H_2O + H^+$$
$$ArOH + H_3AsO_3 \leftrightarrow ArAsO_3^{-2} + H_2O + 2H^+$$

Binuclear As (V) Adsorption

$$2ArOH + H_3AsO_4 \leftrightarrow Ar_2HAsO_4 + 2H_2O$$
$$2ArOH + H_3AsO_4 \leftrightarrow Ar_2AsO_4^- + 2H_2O + H^+$$

Binuclear As (III) Adsorption

$$2\text{ArOH} + \text{H}_3\text{AsO}_3 \leftrightarrow \text{Ar}_2\text{HAsO}_3 + 2\text{H}_2\text{O}$$
$$2\text{ArOH} + \text{H}_3\text{AsO3} \leftrightarrow \text{Ar}_2\text{AsO}_3^{-} + 2\text{H}_2\text{O} + \text{H}^+$$

RESULTS

Effect of pH

The pH measurements were carried out in the pH range 1.7- 8.8 (Fig. 1). It was noted that maximum uptake of the arsenite and arsenate takes place at around pH 3.0. Thus, pH 3.0 was selected for all subsequent studies. Beyond pH 7.0 the adsorption of arsenite and arsenate was almost negligible.

Langmuir Isotherm of Arsenite and Arsenate onto *Nigella sativa* L.

In order to assess the adsorption of arsenite and arsenate over *Nigella sativa* L., Langmuir isotherm models was applied in the entire concentration range from 1×10^{-4} to 1×10^{-3} M at pH 3.0 and at different temperatures 25, 35 and 45°C. The Langmuir equation is the mathematical function most commonly used to describe this process. The Langmuir isotherm can be expressed as:

$$q = X_m\, k_C \times (1+k_C)^{-1} \qquad (2)$$

where, q = amount of arsenite or arsenate adsorbed per unit weight of adsorbent (mg g^{-1}), C = concentration of arsenite or arsenate remaining in solution at equilibrium (mg L^{-1}), k is a constant related to the energy or net enthalpy (k). By plotting q versus C at different temperature as shown in (Fig. 2a, b) a curves are obtained which are linear at low equilibrium concentrations, followed by a curvature (concave to the x-axis) and with an asymptotic tendency to saturation corresponding to monolayer covering. This means that, adsorption isotherms of arsenite and arsenate *Nigella sativa* L. are L-type according to the (Giles *et al*., 1974). Another model of Langmuir adsorption of arsenite and arsenate by *Nigella sativa* L., straight lines were obtained by plotting C/q vs. the equilibrium concentration of As in solution C. The linear form of the Langmuir isotherm equation is represented in Eq. 3. The results concerning arsenite and arsenate adsorption for *Nigella sativa* L. are shown in Fig. 3 and 4.

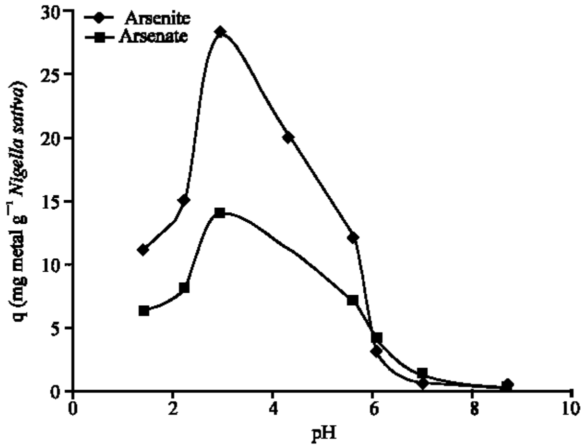

Fig. 1: Effect of pollen adsorption of arsenate and arsenite over *Nigella sativa* L.

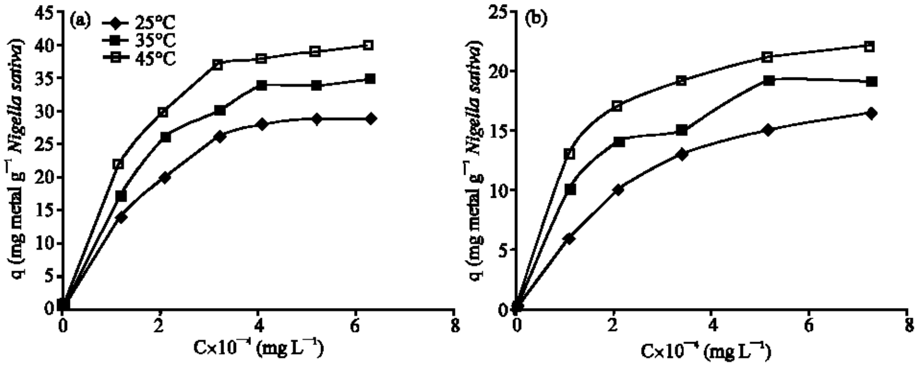

Fig. 2: (a) Langmuir adsorption isotherm of arsenite on *Nigella sativa* L. C vs. q. (b) Langmuir adsorption isotherm of arsenate on *Nigella sativa* L. C vs. q

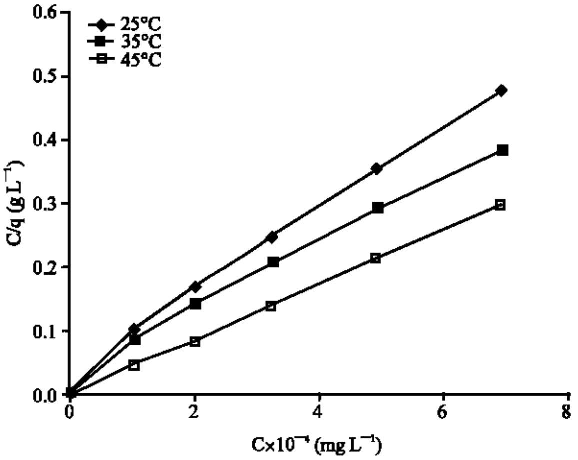

Fig. 3: Plots for langmuir adsorption isotherms of arsenite over *Nigella sativa* L. At different temperature C vs. C/q

Table 1: Binding and thermodynamic parameters for arsenite and arsenate/*Nigella sativa* L. systems

Solution	Temp. (°C)	Xm (mg g^{-1})	K (L mg^{-1})	θ	r	ΔG (kJ mol^{-1})
Arsenite	25	58.34	0.452	0.97	0.995	-44.25
	35	68.92	0.792	0.84	0.935	-41.35
	45	89.21	0.264	0.95	0.982	-39.87
Arsenate	25	96.58	0.548	0.75	0.994	-40.52
	35	62.35	0.185	0.67	1.004	-39.51
	45	68.25	0.264	0.92	0.997	-36.25

$$C/q = 1\times(k\ X_m) + C\times(X_m)^{-1} \tag{3}$$

The values of Xm and k calculated from the slopes and intercepts of the Langmuir plots and correlation Coefficients r, are reported in Table 1. As it can be seen most of the adsorption isotherms fitted the Langmuir equation with correlation coefficients r>0.99. Many experimental isotherms conforming to a Langmuir isotherm involve monolayer coverage. Multiplying Eq. 3 by C gives another modified form (Giles *et al*., 1974):

$$C/r = 1\times(nk)^{-1} + C\times n^{-1} \tag{4}$$

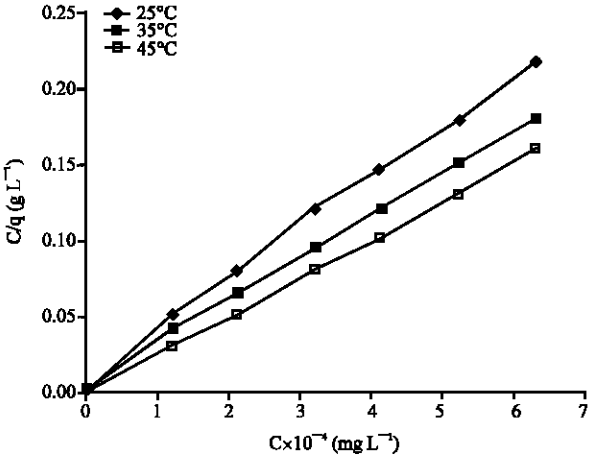

Fig. 4: Plots for langmuir adsorption isotherms for the adsorption of arsenate over *Nigella sativa* L. at different temperature C vs. C/q

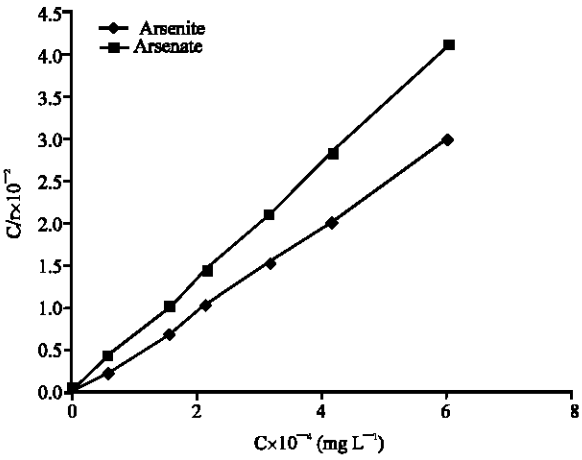

Fig. 5: Langmuir plots of arsenite and arsenate *Nigella sativa* L. systems C vs. C/r

So, that here a Langmuir plot of C/r vs. C should be the straight line slope 1/n, with an ordinate intercept of 1/nK are shown in Fig. 5. Binding parameters were calculated from the intercepts and slopes of Langmuir plots. The derived values of the binding parameters K, θ and r are listed in Table 1. The final column contains the derived values of θ, the maximum fractional occupancy attained experimentally, calculated from the definition of fractional occupancy θ using the value of r at the maximum experimental free metal concentration:

$$\theta = r/n \quad (5)$$

Adsorption free energies (ΔG) of metal adsorbent systems were calculated following equation:

$$\Delta G = -RT \ln K \quad (6)$$

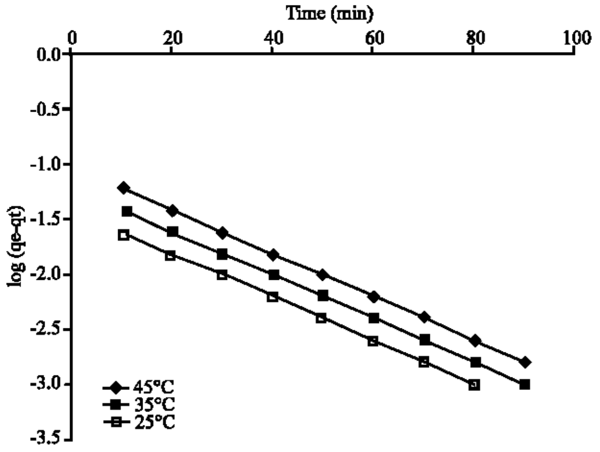

Fig. 6: Lagergren plots for As III *Nigella sativa* L. system at different temperature

Table 2: The slope values of the rate constant, kads at different temperatures for arsenite and arsenate/*Nigella sativa* L. systems

Solution	Temp. (°C)	Slop (min^{-1})
Arsenite	25	4.12×10^{-2}
	35	4.25×10^{-2}
	45	4.37×10^{-2}
Arsenate	25	5.72×10^{-2}
	35	5.84×10^{-2}
	45	5.98×10^{-2}

where, R, T and K are the universal gas constant, the absolute temperature and the equilibrium constant of the adsorption process, respectively. The values of binding parameters calculated from Langmuir binding isotherms and the values of free energy are also given in Table 1.

Calculation of Adsorption Rate Constant

In order to determine specific rate constants of the on-going adsorption following Lagergren's first order rate expression (Penrose and Woolson, 1974) was employed:

$$\mathrm{Ln}\, q_e - q_t = \ln (q_e)\times k_{ad}\times t \qquad (7)$$

where, q_e and q_t are the amount adsorbed at equilibrium and time t, respectively. The plot of time versus log (q_e-q_t) gave straight lines at all the temperatures (Fig. 6). The slope of each straight line gave value of the rate constant, k_{ads} at different temperatures and at 3×10^{-4} mg L^{-1} concentration for arsenite and arsenate and the results given in Table 2. The further increase in values of k_{ads} confirms the increase in uptake of As by increasing temperature.

DISCUSSION

The organic oil contents of *Nigella sativa* L. make it carry a permanent negative charge in their structural framework, this result was supported by Talal and Natsheh (2003) and Mathew *et al.* (2007). The hydration of *Nigella sativa* L. imparts a hydrophilic nature to the mineral surfaces. Because of this property, water is preferentially adsorbed by these surfaces and arsenite and arsenate cannot compete with strongly held water for adsorption sites on the *Nigella sativa* L. surfaces. Adsorption of arsenite and arsenate by *Nigella sativa* L. depends on the amount of the negative aromatic moiety in the *Nigella sativa* L. interlayer sites. It was observed from Fig. 1 that the adsorption of As ion on adsorbent decrease with increase pH at the range 3-7. A continual decrease in the adsorption with a pH increase pH = 3. indicates the possibility of development of positive charge on the *Nigella sativa* L., which inhibits the adsorption of arsenite and arsenate over it these results were contradicted with Teresia and Sylvester (2008), they proved that arsenic removal capacity was increased when the solution pH was increased at pH 8 and above. From Fig. 2a, b, it is interesting to note that values of q_{max} increases with increase in temperature, which indicates the on-going adsorption processes to be endothermic in nature. In this type of isotherm, the initial portion provides information about the availability of the active sites to the adsorbate and the plateau signifies the monolayer formation. The initial curvature indicates that a large amount of arsenite and arsenate is adsorbed at a lower concentration as more active sites of *Nigella sativa* L. are available. As the concentration increases, it becomes difficult for an arsenite and arsenate molecule to find vacant sites and so monolayer formation occurs. The types of system which give this curve do in fact fulfill these conditions. Thus they have one of the following characteristics: (1) the adsorbed molecules are most likely to be adsorbed flat or (2) if adsorbed end-on, they suffer little solvent competition. Examples of (2) are: (a) systems with highly polar solute and adsorbent and a nonpolar solvent and (b) systems with monofunctional ionic substances with very strong intermolecular attraction. It is possible that in the system (b) cases the adsorbed ions may have become associated into very large clusters and just adsorption takes place. Where the sites are few and widely separated, the surface has large hydrophobic regions (Giles ***et al***., 1974). The adsorption rate constant studies gave straight lines at all the temperatures, which confirm the first order nature of the process.

CONCLUSION

The following conclusions can be drawn from this investigation:

- *Nigella sativa* L. can effectively be used for the removal of arsenite As (III) and arsenate (V) ions from waste solution using batch adsorption method. The reaction mechanism was found to be electrostatic attraction between the negatively charged *Nigella sativa* L. and positively charged As ions. The maximum adsorption capacity of arsenite As (III) and arsenate (V) ions reach 28.25 and 12.89 mg g^{-1}, respectively
- Removal of arsenite As (III) and arsenate (V) ions are highly pH dependent, the best results being obtained at pH 3
- Adsorption data of arsenite As (III) and arsenate(V) ions on *Nigella sativa* L. are well described by Langmuir model. Investigations of kinetic models show that first-second-order kinetic model provides better correlation for the experimental data Hence, we can evidently conclude that *Nigella sativa* L. has ability in removing arsenite and arsenate from drinking water, wastewater and ground waster

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