Removal of Arsenic(III) from Drinking Water by Adsorption with Titanium and Ferrous Oxide Nanoparticles

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Adsorption isotherms and reaction kinetics of arsenic(III) removal from drinking water by adsorption with varying amount of titanium and ferrous oxide [namely $Ti(OH)_4$, TiO_2, Fe_3O_4 and Fe_2O_3] were evaluated in the present paper. Arsenic(III) can be average removed over 92 % by these titanium or ferrous adsorbents within 2 h in near neutral solution (include in weak acid and weak alkaline solution). The reaction rate was speedy at initial stage of adsorption but the further time reaction rate was steeply decreased. The removal efficiency of arsenic(III) slightly increased with increasing solution pH to an adsorption maximum at around pH 8 but steep decreased with further increasing solution pH. Adsorption kinetics data were found to be best described by the modified pseudo-second-order kinetics model for titanium adsorbents [$Ti(OH)_4$ and TiO_2] but second-order kinetics model for ferrous oxide adsorbents (Fe_3O_4 and Fe_2O_3). Langmuir and Freundlich isotherms all fit the data but not very well. Maximum adsorption capacity (mg/g) calculated from the slope and the intercept of the graph of Dubinin-Radushkevich (D-R) isotherm were found to be 19.22 mg/g of $Ti(OH)_4$, 4.64 mg/g of TiO_2 and 66.42 mg/g of Fe_3O_4, respectively. Results of adsorption isotherms and reaction kinetics suggested the adsorption of arsenic(III) on titanium and ferrous oxide nano-particles were controlled by chemical process at low concentration but physical in high range.

Key Words: Arsenic(III), Drinking water, Adsorbent, Adsorption isotherms, Reaction kinetics.

INTRODUCTION

Widespread contamination of drinking water with arsenic has been a serious problem, especially in West Bengal, India, Bangladesh, Chile, Vietnam and China. The presence of arsenic in drinking water is mostly due to natural geological processes such as weathering reactions, biological activity and volcanic emissions, as well as anthropogenic activities[1]. Since arsenic is highly toxic and carcinogenic, the WHO, U.S. EPA and a number of countries has revised the guideline for arsenic maximum contaminant level in drinking water from 50 to 10 μg/L. Even, the state of New Jersey of USA proposed that the total arsenic in drinking water should be less than 5 μg/L to ensure the health of people[2].

A number of treatment techniques have been developed for the removal of arsenic from drinking water, namely, coagulation, ion-exchange, adsorption and reverse osmosis. Among various arsenic removal technologies, coagulation and adsorption are believed to be a relative simple, efficiency and cost effective processes[3-5]. Many coagulation and adsorption technologies have been reported to be capable of removing arsenic to levels lower than 50 μg/L, but with the implementation

of revision the permissible levels to 10 μg/L or lower, it is necessary to investigate new treatment approaches or materials that would provide drinking water with arsenic satisfy the maximum contaminant level.

Due to its non-ionic existence as As(III) in natural water, it is generally reported to have low affinity to the surface of various adsorbents or coagulants compared with As(V)[6]. Therefore As(III) is less efficiently removed than As(V) from aqueous solutions by almost all coagulation and adsorption techniques and preoxidation of As(III) to As(V) using some oxidizing chemical agents like chlorine and potassium permanganate is necessary for better removal[7]. However, most arsenic-enriched groundwater is generally dominated by As(III), up to 96 % of total arsenic. Further more, As(III) is more mobile in groundwater and 25-60 times more toxic than As(V)[8].

Nanoparticle TiO_2 and ferrous oxide (include Fe_2O_3 and Fe_3O_4) attracted a lot of research interest as promising arsenic especially arsenite(III) adsorbents because of their high stability, non-toxicity and demonstrated high arsenic removal capability. In the present work, arsenite(III) removal from drinking water by adsorption with several adsorbents of

titanium or ferrous oxide were studied. Adsorption isotherms and kinetics of the adsorption reaction of the As(III) on the these adsorbents were discussed.

EXPERIMENTAL

The titanium and ferrous oxide adsorbents were prepared by a hydrolysis process. A liquid tetrabutyl titanate [$Ti(OC_4H_9)_4$, 99.0 %], $FeCl_2$ and $FeCl_3$ were used in the hydrolysis process as the raw material. Arsenic(III) oxide (As_2O_3, Jingchun Chemical Reagent Co. Ltd., Shanghai) was used to prepare As(III) stock solution and concentrated hydrochloride acid (HCl, 32-38 %) and sodium hydroxide (NaOH, 99 %) were used to stabilize the arsenic species or as precipitant. All the chemicals and materials used were of analytical grade without further purification and purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai except the As_2O_3.

Adsorbent preparation: An aqueous $Ti(OC_4H_9)_4$ of 50 mL was hydrolyzed by drop-wise addition of aqueous NaOH as the precipitator with a rate of 1 mL/min until the pH of the mixture reached 9. The hydrolysis was performed at 20 ºC. The obtained hydrolysis product was white, then rinsed with de-ionized water for 1 h to remove remained organism. After dried at 85 ºC for 12 h, the powder was white and denoted as $Ti(OH)_4$. Then the white powder was calcined in ambient atmosphere at 400 ºC for 2 h and denoted as TiO_2.

The preparing procedures of ferrous oxide adsorbents were detailed as follows: Firstly, the mixed solution of $FeCl_2 \cdot 4H_2O$ (0.100 mol/L) and $FeCl_3 \cdot 6H_2O$ (0.100 mol/L) was prepared by dissolving 1.988 g $FeCl_2 \cdot 4H_2O$ and 2.703 g $FeCl_3 \cdot 6H_2O$ together in 100 mL deionized water. The NaOH solution (0.200 mol/L) was prepared by dissolving 0.80 g NaOH in 100 mL deionized water. Then, the two solutions were mixed sufficiently with equal volumes. The precipitate was dried at 85 ºC for 12 h, the powder was black and denoted as Fe_3O_4. Then the black powder was calcined in ambient atmosphere at 400 ºC for 2 h. Then the colour of the powder was changed from black to red and denoted it as Fe_2O_3. All the obtained adsorbent was ground to fine powder in an agate mortar for use.

Arsenic sorption experiments: The adsorption experiments for As(III) removal by varying amount of adsorbents were determined in batch reactors. By adding 0.015, 0.025, 0.05, 0.10, 0.20 and 0.50 g of adsorbents into 100mL glass bottles contaminated 1.00 mg/L As(III). Suspension settle in sealed homoeothermic incubator, shake velocity at 60 rpm.

Experiments to determine adsorption rates and kinetics were carried out by adding 0.200 g of adsorbents into 1000 mL glass bottles contaminated 1.00 mg/L As(III). Before adding the adsorbent, As(III) solution was heated to designated temperature. Suspension settle in sealed homoeothermic incubator, shake velocity at 60 rpm.

Adsorption isotherms were obtained by adding different amounts of absorbent into 100 mL As(III) solutions initial concentration at 1.00 mg/L. The temperature was control at 25 ºC. After 24 h of mixing, suspension samples were withdrawn and filtered through 0.45 µm filter film.

The pH of the solutions was adjusted with HCl and NaOH to designated values (about pH = 7) by using a potential meter

(FE20, Mettler Toledo Instrument Co. Ltd.) in above experiments. After an aliquot was sampled, filter the sample immediately through 0.45 µm filter film (Millipore Corporation, USA). Variations in the concentration of As(III) of each particle-removed sampled solution were monitored using atomic absorption spectrophotometer (TAS-990, Beijing Puxi Instrument Co. Ltd.) with an As hole cathode lamp. A hydride generation system was connected to the equipment and the arsine was atomized in a quartz cell.

RESULTS AND DISCUSSION

Effect of absorbent dosage: The removal efficiency of arsenic by adsorption reaction of As(III) solution was investigated with different initial concentrations of varying amount of adsorbents (0.15-5 g/L). Fig. 1 shows that the concentration of As(III) decreased with higher concentrations of varying amount of adsorbents. As(III) can be removed over 85 % when dosage of Fe_2O_3 or $Ti(OH)_4$ was 1 g/L. Removal efficiency can only slightly increased with increasing adsorbent dosage when dosage over 1 g/L, for example, removal efficiency increased from 33.4 % to 85.6 % with the dosage of $Ti(OH)_4$ increasing from 0.2 g/L to 1.0 g/L, but from 85.6 % to 96.9 % with the dosage increasing from 1.0 g/L to 5.0 g/L. The As(III) can be removed over 92 % by these titanium or ferrous adsorbents within 2 h suggested As(III) can be treated well by adsorption process. Lackovic *et al.*[9] used zero-valent iron as an adsorption medium and observed more than 95 % of arsenic removal efficiency in both the laboratory and field column studies. But few literatures had reported As(III) in high-arsenic contaminated groundwater can be treated to satisfy the maximum contaminant level just by adsorption technique alone if without other assistant process such as pre-process or co-process[3,10]. The residual As(III) in the solution far exceed the arsenic standard (10 µg/L in drinking water) even the dosage over 5 g/L may suggest there should be co-technique using when these adsorbents application in drinking water purification if the initial concentration of As(III) is very high.
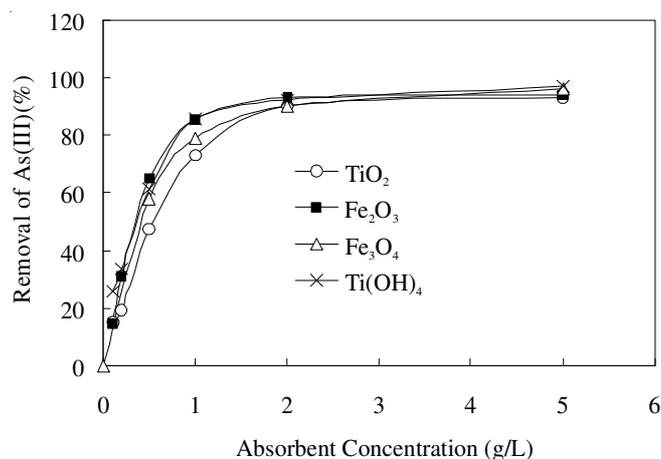
Fig. 1. Effect of adsorbent concentration on As(III) adsorption from solution by varying amount of adsorbents, with reaction conditions: contact time = 2 h, initial As concentration = 1.00 mg/L

Effect of pH: Effect of pH on As(III) adsorption by varying amount of adsorbents were shown in Fig. 2. The removal

efficiency of As(III) in near neutral solution (include in weak acid and weak alkaline solution) may indicate existence in non-ionic H_3AsO_3 in neutrally water doesn't suppress contact of As(III) with the experimented adsorbents. This result may indicate strong binding force between the non-ionic H_3AsO_3 and the adsorbents could be achieved in the adsorption process. But the removal of As(III) decreasing obviously when pH of solution decreased from 6 to 3. The As(III) species in form of H_3AsO_3 almost 100 % with pH value less than 7. The decreased effect with decreasing pH may caused by surface properties changed in the acid conditions.
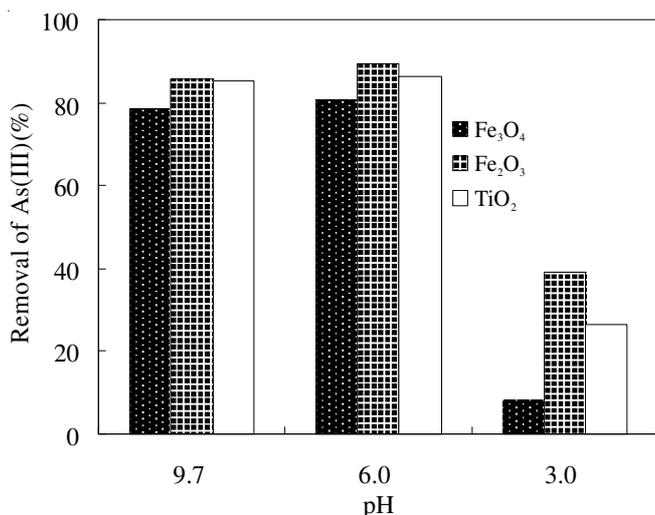
Fig. 2.   Effect of pH on As(III) adsorption from solution by varying amount of adsorbents, with reaction conditions: contact time = 2 h, initial As concentration = 1.00 mg/L, adsorbent dosage = 2.0 g/L

In order to evaluate effects of pH on As(III) adsorption, further experiments conduct on titanium dioxide under different pHs were performed. The results were shown in Fig. 3. The experimental observations showed that modified pseudo-second-order kinetics constants of As(III) removal slightly increases with increasing solution pH to an adsorption maximum around pH 8 and steep decreases with further increases in solution pH. Similar As(V) adsorption behaviours were observed before[11,12].
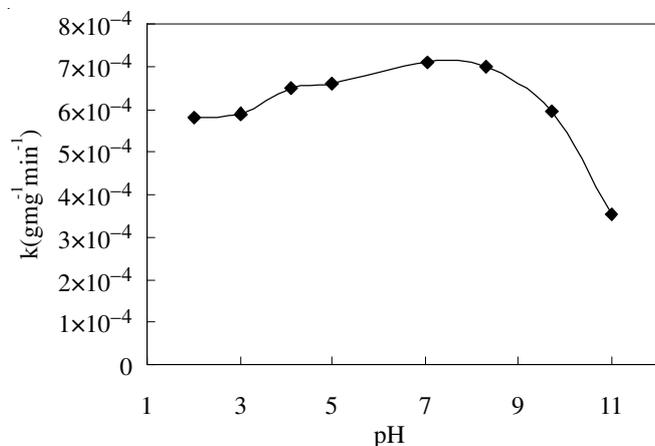
Fig. 3.   Effect of pH on As(III) adsorption from solution by TiO$_2$ adsorbent, with reaction conditions: contact time = 2 h, initial As concentration = 0.150 mg/L, adsorbent dosage = 0.2 g/L

The pKa$_1$, pKa$_2$ and pKa$_3$ values of H_3AsO_3 are 9.22, 12.3 and 13.4, respectively, so, As(III) predominately exists as H_3AsO_3 when pH is in the range of 2-7[13]. Relatively higher adsorption of As(III) in the pH range 2-7 can be attributed to surface complexes formed but not the electrostatic attraction between the H_3AsO_3 and positively charged surface of TiO_2 ($H^+ + Ti-OH \rightarrow Ti-OH_2^+$, pKs = 4.58). Whereas the decrease in adsorption when pH > 7 can be attributed to electrostatic repulsion between $AsO(OH)_2^-$ and the negatively charged surface of TiO_2($OH^- + Ti-OH \rightarrow Ti-OOH_2^-$). Pena and Jing et al.[14] had reported the surface complexes formed between TiO_2 and arsenic species and maintained the non-protonated speciation at pH values from 5 to 10 and the dominant surface species were $(TiO)_2AsO_2^-$ and $(TiO)_2AsO^-$ for As(V) and As(III), respectively. Otherwise, the pH increase led to the dramatic decrease of As(III) removal rate in alkaline solution (pH > 9) was also attributed to decrease of numbers of positively charged active sites on particle surfaces and to the increase in numbers of OH^- ions competitive with arsenic for adsorption on titanium dioxide surface.

Reaction kinetics: The effect of contact time (10-120 min) on arsenic adsorption in As(III) batches reactor is shown in Fig. 4. The results clearly demonstrate that adsorption efficiencies increased rapidly with an increase in contact time up to 20 min and maximum removal of 91.8, 93.6 and 96.5 % were achieved with a contact time of 120 min by Fe_3O_4, Fe_2O_3 and TiO_2, respectively. Most of As(III) in the solution can adsorb onto the adsorbents in a short time, about 80 % of As(III) be removed less than 40 min. The reaction rate was very speedy at initial stage of adsorption but was steeply decreased in the further time. Xu et al.[8] had reported most of the As(III) in the solution was adsorbed onto $TiO_2 \cdot xH_2O$ nano-particles in a short time, e.g., around 52 % As(III) in the solution was adsorbed in just 15 min when the $TiO_2 \cdot xH_2O$ loading concentration was just 0.04 g/L (40 ppm). Guo et al.[6] reported equilibrium adsorption time need more than 190 h when they using natural siderite as the adsorbent to remove arsenic(III) and arsenic(V) from groundwater. This may indicate rapid reaction rate in the initial stage of reaction can be archived in the adsorption process treated by these titanium or ferrous compound adsorbents.

The As(III) adsorption kinetics data were found to be best described by the modified pseudo-second-order kinetics model(Fig. 5a and b) for titanium adsorbent [Ti(OH)$_4$ and TiO$_2$], which can be described by eqn. 1.

$$\frac{1}{Q_e - Q_t} - \frac{1}{Q_e} = k \cdot t^n \qquad (1)$$

where, Q_t is amount of As(III) adsorbed at time t, where Q_e is amount of As(III) adsorbed at equilibrium time and k and n are rate constant and order respectively[8,15]. In a general pseudo-second-order kinetics model, n in the equation was 1. A number of power-function kinetic models which expressed by eqn. 2 were reported in heterogeneous systems[13,16].

$$Q_t = k \cdot t^n \qquad (2)$$

At the initial stage of adsorption, adsorption rate approximately direct proportionality to concentration of dissolved As(III) in solution, thus, first-order reaction model or pseudo-
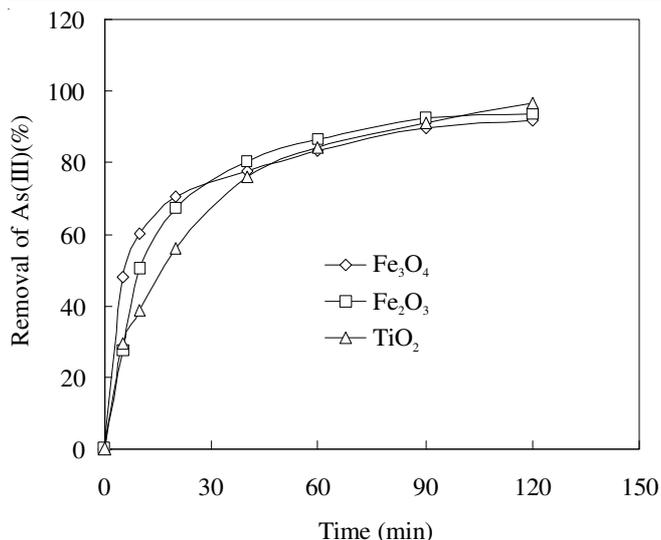
Fig. 4. Effect of contact time on As(III) adsorption from solution by varying amount of adsorbents, with reaction conditions: initial As concentration = 1.00 mg/L, adsorbent dosage = 2.00 g/L

sufficient with the chemical adsorbed H_3AsO_3. further adsorption on multiple-layer coverage of homogeneous surface may happen through physical process by van der Waals force.

first-order reaction model may described adsorption kinetics data. When adsorption process almost reached equilibrium state, apparent adsorption rate decreased to 0 whatever the concentration of residual As(III). Thus, kinetic model may appear in reaction rate with a function of time, this was often occurred in a heterogeneous system especially reaction control by diffusion within pores. Data were tested by least-square regression analysis and correlation coefficient (R^2) of modified pseudo-second model were 0.9917 and 0.9882 at 298 K, 0.9793 and 0.9892 at 323 K for $Ti(OH)_4$ and TiO_2, respectively. The closeness of R^2 to 1 indicates that the model fitted the experimental data accurately. In each case, the high coefficient of determination value ($R^2 > 0.98$) suggests that the uptake of arsenic (III) varies almost linearly with $t^{0.5}$, which reflects the characteristics of intraparticle diffusion[17,18]. This suggests that the adsorption of As(III) on these titanium adsorbents was governed by the diffusion within pores of the adsorbent. Badruzzaman *et al.*[19] observed similar results during the adsorption of arsenic (V) onto granular ferric hydroxide.

The adsorption kinetics data were found to be best described by the second-order kinetics model (Fig. 5c) for ferrous oxide adsorbent (Fe_3O_4 and Fe_2O_3), which can be described by the eqn. 3.

$$\frac{1}{C_t} - \frac{1}{C_0} = kt \qquad (3)$$

where, C_t is concentration of As(III) in solution at time t, C_0 is initial a concentration of As(III) in solution[20]. A plot of $(1/C_t-1/C_0)$ *versus* t for the adsorption under consideration is shown in Fig. 5. The correlation coefficient (R^2) were 0.9299 for Fe_2O_3, 0.9902 for Fe_3O_4 indicates that the adsorption followed the second-order reaction model well. The reaction rates were speedy at initial stage of adsorption but the further time reaction was steeply decreased. This indicates the adsorption reaction may divide into two separated process. The initial adsorption was controlled by chemical adsorb which occurred between H_3AsO_3 and these titanium and ferrous oxide nano-particles. After monolayer surface of the adsorbent was
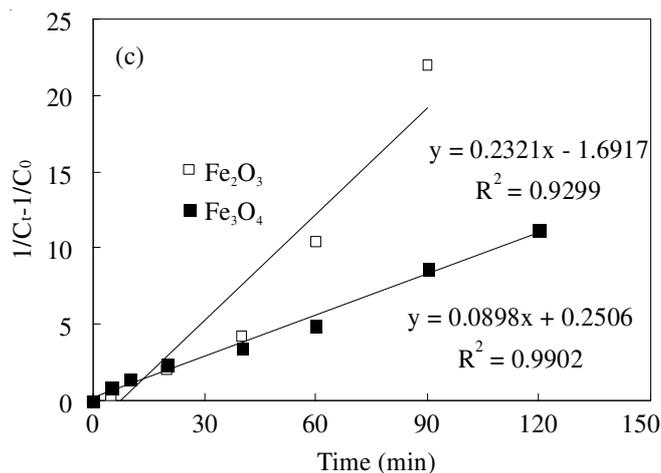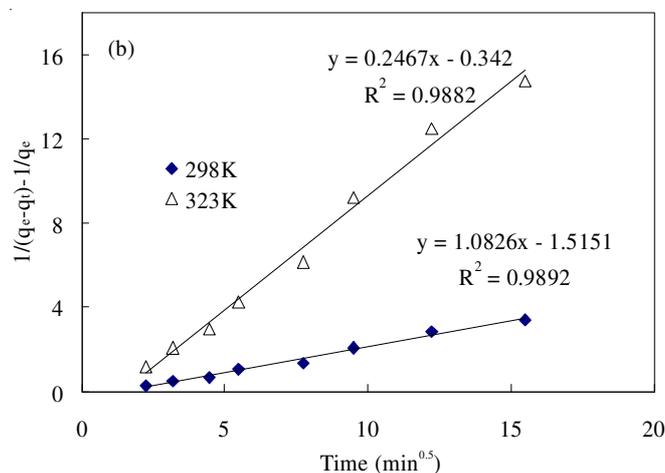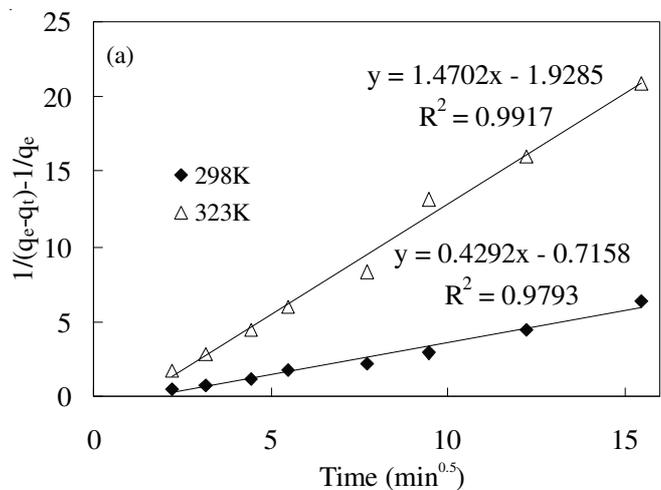
Fig. 5. Second-order (c) and modified pseudo-second-order (a, b) kinetics model of the reaction of As(III) adsorption from solution by varying amount of adsorbents, with reaction conditions: initial As concentration = 1.00 mg/L, adsorbent dosage = 2.00 g/L. (a) $Ti(OH)_4$, (b) TiO_2, (c) Fe_2O_3, Fe_3O_4

Adsorption isotherms: Langmuir isotherm model assumes a monolayer surface coverage limiting the adsorption due to the surface saturation, while the Freundlich isotherm

model is an empirical model allowing for multilayer adsorption[6]. Langmuir adsorption isotherm equation can be expressed by the eqn. 4.

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m b} \cdot \frac{1}{C_e} \qquad (4)$$

where, Q_e is the specific adsorbed quantity of a model pollutant compound and C_e is the concentration of which, both at equilibrium; Q_m is the saturation (maximum) adsorption capacity and b is the ratio of K_a/K_d, K_a is the adsorption constant and K_d is the de-sorption constant. Freundlich adsorption isotherm equation can be expressed by the eqn. 5.

$$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (5)$$

where, K_f and n are two Freundlich isotherm parameters.

Equilibrium adsorption of As(III) by varying amount of adsorbents was shown in Fig. 6 and Langmuir isotherm model in Fig. 7 while Freundlich isotherm model was shown in Fig. 8. The respective empirical constants for the Langmuir and Freundlich isotherm models along with correlated coefficients (R^2) were presented in Table-1. The R^2 values obtained from the Langmuir isotherm were 0.932, 0.984 and 0.928 of Ti(OH)$_4$, TiO$_2$ and Fe$_3$O$_4$, respectively. The R^2 values obtained from the Freundlich isotherm were 0.934, 0.943 and 0.963 of Ti(OH)$_4$, TiO$_2$ and Fe$_3$O$_4$, respectively. These results indicated that the Langmuir isotherm and Freundlich isotherm all fit the data but not very well. These may indicate adsorption of As(III) onto theses titanium and ferrous oxides due to complex actions of monolayer and multiple-layer coverage on homogeneous surface.
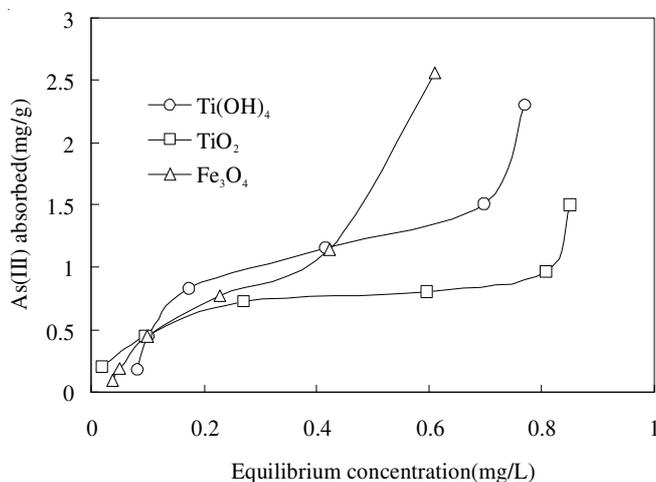
Fig. 6.　Equilibrium adsorption of As(III) by vary adsorbents, with reaction conditions: initial As concentration = 1.00 mg/L, contact time = 2 h

TABLE-1
CORRELATION COEFFICIENT (R^2) OF LANGMUIR AND FREUNDLICH ISOTHERMS MODEL OF ARSENIC(III) ADSORPTION ON VARY ADSORBENTS

Isotherm	Ti(OH)$_4$	TiO$_2$	Fe$_3$O$_4$
Langmuir	0.932	0.984	0.928
Freundlich	0.934	0.943	0.963
Dubinin–Radushkevich	0.930	0.938	0.957

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[21,22], which can be expressed as eqn. 6.

$$\ln Q = \ln Q_m - k\varepsilon_2 \qquad (6)$$

where, ε (polanyi potential) can be expressed as:

$$\varepsilon = RT \ln[(1 + (1/C_e)]$$

In the above equation, Q is the amount of arsenic adsorbed at equilibrium per unit weight of adsorbent (mg/g), Q_m is the maximum adsorption capacity (mg/g), C_e the equilibrium concentration of arsenic in the solution (ppm), k the constant related to adsorption energy (mol^2 kJ^{-2}), R is the gas constant (kJ mol^{-1} K^{-1}) and T the temperature (K). D-R isotherm was drawn by plotting lnQ against ε^2 (Fig. 9). Q_m and k were calculated from the slope and the intercept of the graph and found to be 19.22 mg/g and -0.049 mol^2 kJ^{-2} of Ti(OH)$_4$, 4.64 mg/g and -0.0309 mol^{2}kJ^{-2} of TiO$_2$, 66.42 mg/g and -0.0679 mol^2 kJ^{-2} of Fe$_3$O$_4$, respectively, where k was independent of temperature.
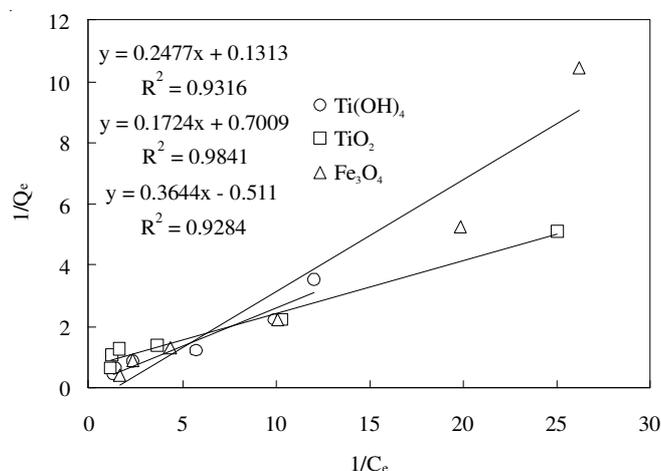
Fig. 7.　Langmuir isotherm model for arsenic adsorption on titanium and ferrous oxide adsorbents
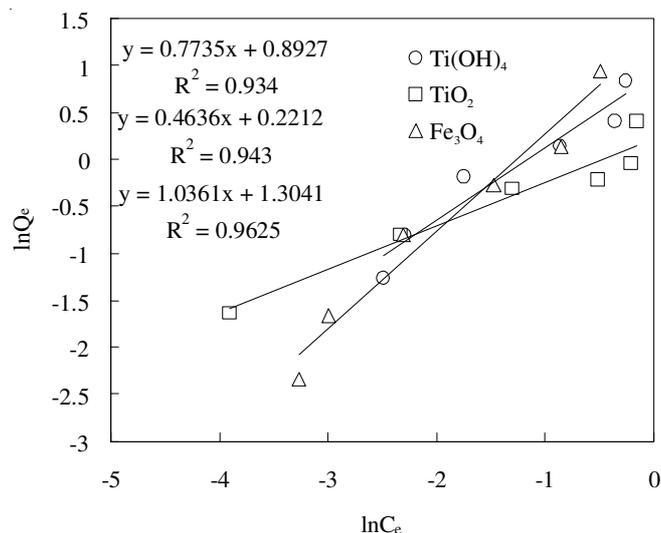
Fig. 8.　Freundlich isotherm model for arsenic adsorption on titanium and ferrous oxide adsorbents

The mean free energy of adsorption (E), defined as free energy change when 1 mol of ion is transferred from solution to the surface of the adsorbent, was calculated from the k-value using the following eqn. 7:[15,20]

$$E = (-2K)^{-0.5} \qquad (7)$$

If the value is more than 8 kJ mol^{-1}, the adsorption type is considered as chemical reaction; and if it is = 8 kJ mol^{-1}, then the adsorption is physical. The values of E found in this study were 3.19, 4.02 and 2.71 kJ mol^{-1} for Ti(OH)$_4$, TiO$_2$ and Fe$_3$O$_4$, respectively. This indicates that the adsorption is physical in nature. The adsorption of As(III) on titanium and ferrous oxide nano-particles were controlled by chemical process at initial stage but physical at latter as mentioned above. Most of the As(III) were chemical adsorbed on surface of adsorbent when equilibrium concentration is very low. If the equilibrium concentration of As(III) in solution exceed a critical point the adsorption should occurred in physical process. The calculated maximum adsorption capacity of As(III) on the adsorbents by D-R isotherm shows the adsorption is physical in nature may indicate only very few chemical adsorbed As(III) molecular which can be neglect in the isotherm.
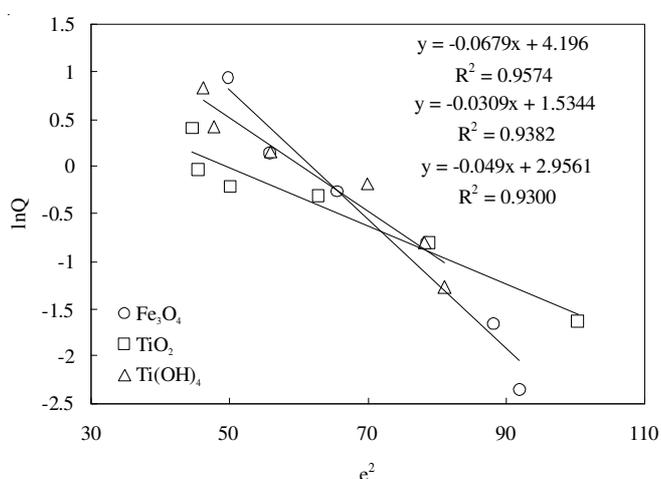
Fig. 9.   Dubinin-Radushkevich isotherm model for arsenic adsorption on titanium and ferrous oxide adsorbents

Conclusion

Most of the As(III) in the solution can adsorb onto the adsorbents in a very short time, about 80 % of As(III) be removed less than 40 min. The adsorption was evaluated by the Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. Maximum adsorption capacity (mg/g) of the evaluated adsorbents caculated by D-R isotherm were 19.22, 4.64 and 66.42 mg/g of the Ti(OH)$_4$, TiO$_2$ and Fe$_3$O$_4$, respectively. The adsorption mechanism follows the modified pseudo-second-order reaction kinetics and the pores diffusion is the rate-limiting step. Results of adsorption isotherms and reaction kinetics suggested the adsorption of As(III) on titanium and ferrous oxide nano-particles were controlled by chemical process chemical process at low concentration but physical in high range.

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