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ADSORPTION OF Se(IV) AND Se(VI) ON AN IRON-COATED SAND FROM WATER

Shang-Lien Lo* and Tsung-Yung Chen

Graduate Institute of Environmental Engineering
National Taiwan University, 71 Chou-Shan Rd.
Taipei, Taiwan, R.O.C.

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ABSTRACT

This study was aimed at developing a method for coating hydrated iron-oxide onto the surface of quartz sand. Two coating parameters were investigated: the pH at which iron-oxide was synthesized and the coating temperature. According to the results, a larger quantity of iron was coated onto quartz sand in the lower pH range (0.5 - 2.0). This iron-oxide-coated sand (IOCS) produced at low pH was more difficult to dissolve in acidic and basic solution and had better Se(IV) and Se(VI) adsorption efficiencies than did IOCS produced at high pH (8.0 - 11.0). Adsorption experiments showed that Se(IV) adsorption by IOCS was specific and Se(VI) adsorption was nonspecific. In kinetic experiments, pseudo-equilibrium of Se(IV) adsorption was attained within 10 minutes while Se(VI) adsorption needed 1.5 hours. Higher concentrations of NaOH solution could increase the desorption rate of Se(VI) but could not increase the total desorbed quantity. In addition, adsorption isotherm results indicated that the adsorption capacity of IOCS from pH 4.0 to 6.5 was 0.014 - 0.017 mmole Se / g sand for Se(IV) and was 0.013 - 0.014 mmole Se / g sand for Se(VI).

Key words: Adsorption, coatings, hydrated iron oxide, sand, selenate, selenite.

INTRODUCTION

Selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), elemental selenium, and selenide are four species of selenium that exist in soil, whereas Se(IV) and Se(VI) dominate in aqueous systems. Elemental selenium poses no risk to humans. However, selenium oxide, selenium trioxide, and hydrogen selenide have been verified to be public health hazards. Selenite is hard to dissolve in water and easily adsorbed by soil colloids including Fe and Al oxides. As a result, selenate becomes the major species of selenium in water. The selenium concentration in natural water bodies is usually under 3 μg/L. It is certain that water is polluted by industrial wastewater when selenate or selenite appears in high concentrations.

Iron oxides are abundant in soil and water environments. In comparison with other minerals existing in soil, they have relatively high surface areas and surface charges, and they often regulate free metal concentrations in soil through adsorption reactions [1]. Many researchers have studied the adsorption characteristics of anions, cations, and organics onto the iron oxide surface in recent decades. Adsorption is capable of removing metals over a wider pH range and to much lower concentrations than precipitation [2]. Schultz *et al.* [3] and Edwards & Benjamin [4] investigated the feasibility of reusing iron hydroxide adsorbents and concluded that iron oxide could be regenerated and reused at least 50 times without a noticeable loss in treatment efficiency. However, most iron oxides are available only as fine powders or are generated in aqueous suspension as hydroxide floc or gel. In such forms, these oxides retain their desirable adsorptive properties for trace metals but are limited to reactor configurations incorporating large sedimentation basins or filtration units, which causes solid/liquid separation to become fairly difficult. Furthermore, iron oxide alone is not suitable as a filter medium because of its low hydraulic conductivity [5].

Recently, several researchers have developed techniques for coating iron oxide onto the surface of sand to overcome the problem of using iron oxide powders in water treatment. Iron-coated sand has been tested for removal of cationic as well as anionic metals from synthetic and real wastes [6-10]. The results from these studies confirm that the utilization of iron-coated sand for trace element removal from water is worth developing. The applications of iron-coated sand are influenced by the coating techniques. Iron oxide formed from $Fe(NO_3)_3$ is composed of mainly amorphous iron oxides and a small amount of crystalline iron oxides [11, 12]. But the type of iron oxide coating produced depends on the physical and chemical environments at which iron oxide was prepared and coated.

MATERIALS AND METHODS

Coating Process

Stock solution of 0.5 M Fe(III) was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in Milli-Q water. Sand was selected from 16 to 25 mesh sieves (0.67 to 0.99 mm in diameter), pretreated in HCl solution (pH 1.0) for 24 hrs, rinsed with de-ionized water, and dried at 103°C. To coat the sand, stock solution of 0.5 M Fe(III) and Milli-Q water were added to a 1200-ml beaker to obtain a 1-liter solution with the required concentration of iron ion. Base (3.0 N or 0.01 N NaOH) was added dropwise until the desired pH was attained. The solution was continuously stirred for about 10 mins to create an iron oxide floc suspension. Then, sand (200 g) was placed in the beaker with the iron oxide floc suspension. The beaker was heated and stirred in an oven for 24 hrs. After that, the coated sand was washed with de-ionized water until the runoff was clear, and then it was redried in the oven for 5 hrs. The final iron-oxide-coated sand (IOCS) was stored in polystyrene bottles until further use.

To measure the total iron on the surface of the coated sand, 5 g of IOCS was soaked in 6 N HCl solution (50 ml) for 24 hrs. After the iron was dissolved completely, the solution was vacuum-filtered through a 0.2 μm membrane filter (MFS product, USA). The sand was rinsed with 70 ml of 1:20 HCl solution during filtration to remove the remaining iron. The quantity of Fe in the filtrate was determined by atomic absorption spectrophotometry (Perkin-Elmer 5000). A quantitative analysis of the attachment strength was performed by measuring the amount of iron dissolved when a suspension of IOCS (pH 2.0 and pH 13.0) was placed in an end-over-end roller operating at 10 rpm for 3 hrs.

Se-Adsorption Experiments

Stock solutions of 1000 mg/l Se(IV), Se(VI), and Se(IV) + Se(VI) were prepared by dissolving Na_2SeO_4 and Na_2SeO_3 in Milli-Q water. Adsorption experiments included both of the equilibrium and kinetic studies. Adsorption studies in batch were carried out in Pyrex vessels with agitation provided by stirring mixers. The temperature was controlled at 20°C by circulating water from a temperature bath, and carbon-dioxide-free nitrogen was bubbled through these vessels. A 100-ml solution containing 10 mg/l Se(IV), Se(VI), or Se(IV) + Se(VI), was adjusted to a background ionic strength of 0.0001 - 0.01N with $NaNO_3$ or Na_2SO_4. A fixed amount of IOCS (10 g) was added to the solution and its pH adjusted to the desired value with 0.1 N HNO_3 and 0.1 N NaOH. After a specified time, solid and liquid were separated by a 0.2 μm membrane filter. Residual Se concentration of filtrate was determined by ion chromatography (IC, Dionex, 2000i/SP).

In the adsorption equilibrium experiments, the pH of the solution was 6.5, and the reaction time was 3 hrs. In addition, a control test was conducted with uncoated sand in order to compare the Se adsorption capability of the coated sand with the uncoated sand. In the adsorption rate experiments, the reaction time lasted 36 hrs with the solution pH maintained at 6.5. The supernatant from the equilibrium experiments was then discarded for the following Se-desorption rate experiments, in which samples were taken at specified time intervals after adding 100 ml of 0.01 N or 0.1 N NaOH to the vessels. The adsorption isotherm experiments were conducted in 100-ml flasks by adding 5 g IOCS into 50-ml solutions of different Se concentrations (100 - 1000 mg/l) under two solution pH values (4.0 and 6.5). The flasks were shaken at 100 rpm for 3 hrs, the solution filtered, and the residual Se concentration analyzed by IC.

RESULTS AND DISCUSSION

Evaluation of Coating Methods

Figure 1 shows the amount of iron coated per unit weight of sand for different coating conditions. The pH (0.5 - 11.0) at which iron oxide was prepared and the coating temperature (105°C, 200°C) are expressed as $pH_{(coating)}$ and $temp_{(coating)}$, respectively. No significant difference was evident between the amount of iron coated at 105°C and 200°C. However, $pH_{(coating)}$ significantly influenced the coating results. When pH < 2.0, the IOCS contained more iron oxide. The coating formed at pH = 1 contained the maximum amount of iron. When $pH_{(coating)}$ was between 8.0 and 11.0, the amount of coated iron was relatively lower. Most iron oxides in pre-coating solution are very tiny, suspended floc when $pH_{(coating)}$ is lower than 2.0, but in a solution with $pH_{(coating)}$ at 8.0 - 11.0, they exist as large floc, look like slurry, and are hard to coat onto quartz sand. Generally, the amount of iron coated is about 4 - 10 mg Fe / g sand.

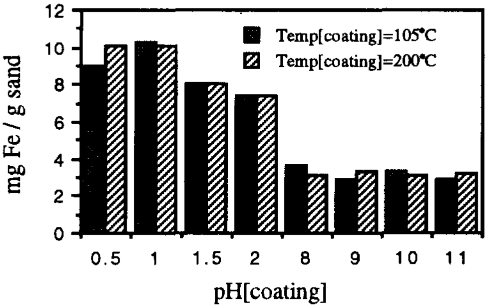

Fig. 1. Amount of iron coated per unit weight of sand

Acid- and alkali-resistance tests were conducted by soaking IOCS in HCl solution (pH=2.0) and NaOH solution (pH=13.0) for 3 hrs, respectively. Figures 2 and 3 indicate the results. The $pH_{(coating)}$ has significant influence on attachment strength. The amount of iron dissolved from coatings produced at higher $pH_{(coating)}$ was greater than that produced at lower $pH_{(coating)}$ because most iron oxides exist as solid precipitates at higher $pH_{(coating)}$. Even at different $temp_{(coating)}$, much more iron was dissolved from high-$pH_{(coating)}$ coatings. Furthermore, a higher temperature (200°C) provided more energy to build a stronger bond between iron oxide and quartz sand. Thus, IOCS produced at higher $temp_{(coating)}$ was more resistant to acid / alkali. Lo *et al.* [10] made a similar conclusion and pointed out that coatings formed at 500°C were much stronger (8-10 times) than those formed at 60°C.

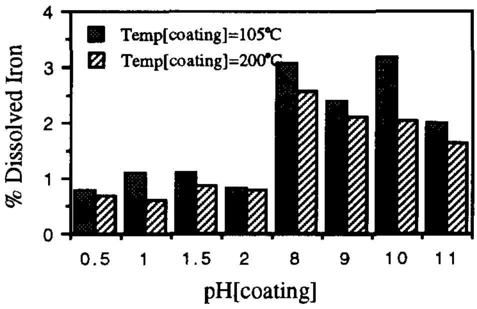

Fig. 2. Acid-resistance of IOCS (pH=2, HCl, 3 hrs)

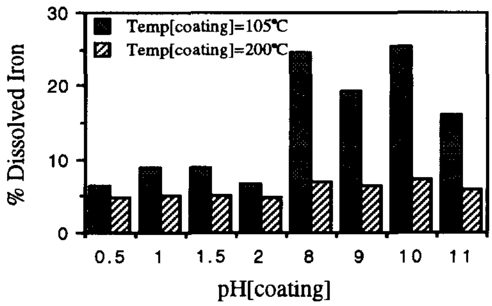

Fig. 3. Alkali-resistance of IOCS (pH=13, NaOH, 3 hrs)

Effect of $pH_{(coating)}$ on Se-adsorption

The results of the control test indicated that the uncoated quartz sand could adsorb neither Se(IV) nor Se(VI), meaning that IOCS adsorption of Se occurred on the iron oxide surface. The results of the batch adsorption experiments are shown in Figs. 4-7. The adsorption efficiencies of Se(IV) and Se(VI) onto IOCS formed at lower $pH_{(coating)}$ were better than those of IOCS produced at higher $pH_{(coating)}$. The iron oxide coating of the IOCS formed at low $pH_{(coating)}$ possessed more H^+ on its surface and carried a positive charge; consequently, they easily adsorbed anions such as Se(IV) and Se(VI). However, the amount of anions adsorbed by the IOCS does not represent its adsorption capacity. For instance, IOCS formed at low $pH_{(coating)}$ contained more iron on its surface, allowing it to adsorb more anions. Thus, the ratio of adsorbed Se to iron coated on the IOCS surface (mmole adsorbed Se / g Fe) should be used as the index for adsorption density.

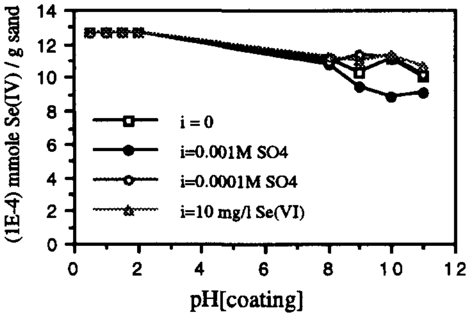

Fig. 4. Adsorption of Se(IV) on IOCS ($temp_{(coating)}$ 105°C, C_0=10 mg/l, pH 6.5)

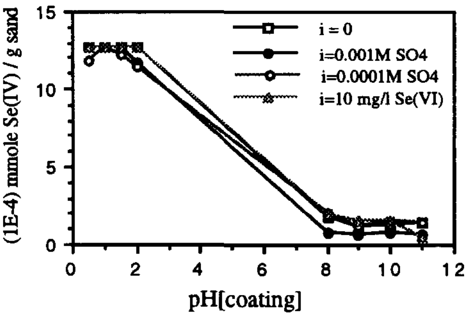

Fig. 5. Adsorption of Se(IV) on IOCS ($temp_{(coating)}$ 200°C, C_0=10 mg/l, pH 6.5)

Figures 8-11 show adsorption density comparisons for Se(IV) and Se(VI). All of the results, except those in Fig. 8, indicate that IOCS produced at low $pH_{(coating)}$ have larger adsorption densities. In the Se-adsorption tests, all IOCS produced at low $pH_{(coating)}$ and $temp_{(coating)}$=105°C could adsorb Se(IV) completely, that is, this kind of IOCS could adsorb more Se(IV) than the amount supplied in the experiments. The results of Se(IV) adsorption isotherms also showed that its Se(IV) adsorption capacity was about 20 times that of IOCS coated at low $pH_{(coating)}$. Therefore, the smaller Se(IV) adsorption density of IOCS produced at low $pH_{(coating)}$ was due to an insufficient number of Se(IV) ions. In general, IOCS produced at low $pH_{(coating)}$ had larger adsorption densities for Se(IV) and Se(VI) than those formed at high $pH_{(coating)}$.

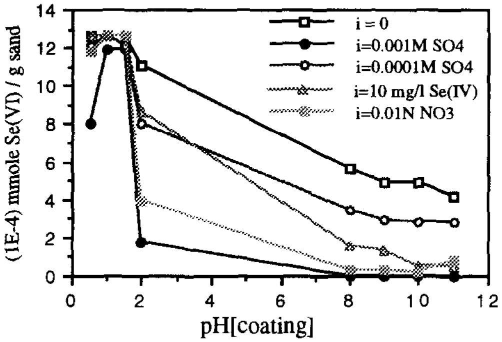

Fig. 6. Adsorption of Se(VI) on IOCS ($temp_{(coating)}$ 105°C, C_0=10 mg/l, pH 6.5)

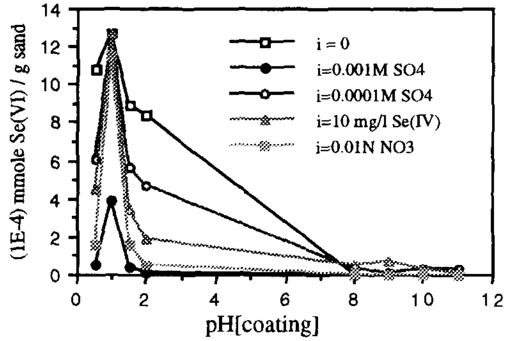

Fig. 7. Adsorption of Se(VI) on IOCS ($temp_{(coating)}$ 200°C, C_0=10 mg/l, pH 6.5)

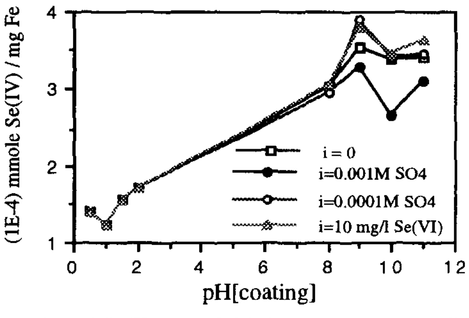

Fig. 8. Adsorption densities of Se(IV) on IOCS ($temp_{(coating)}$ 105°C, C_0=10 mg/l, pH 6.5)

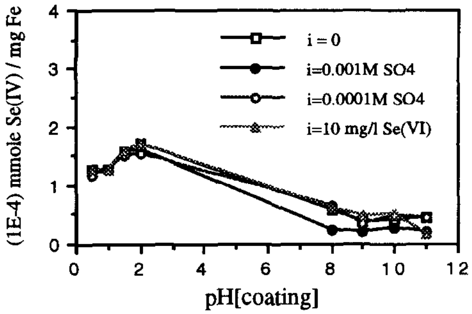

Fig. 9. Adsorption densities of Se(IV) on IOCS (temp$_{(coating)}$ 200°C, C_0=10 mg/l, pH 6.5)

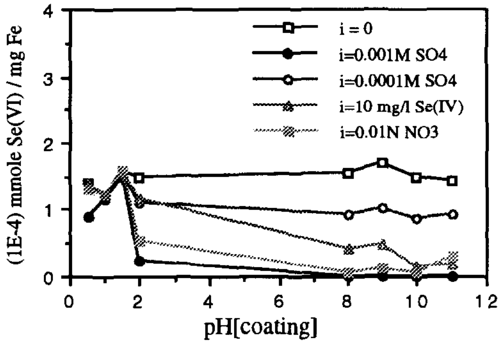

Fig. 10. Adsorbing densities of Se(VI) on IOCS (temp$_{(coating)}$ 105°C, C_0=10 mg/l, pH 6.5)

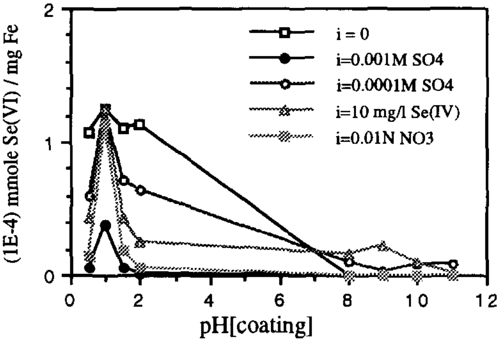

Fig. 11. Adsorption densities of Se(VI) on IOCS (temp$_{(coating)}$ 200°C, C_0=10 mg/l, pH 6.5)

Effect of Temp$_{(coating)}$ on Se-adsorption

Sand coated with iron oxide at 105°C produced better adsorption results for Se(IV) and Se(VI) (Figs. 4 and 6) and had very high, up to 0.0004 mmole Se(IV) / mg Fe and 0.00016 mmole Se(VI) / mg Fe (Figs. 8 and 10), Se adsorption densities. Nevertheless, the adsorption densities for sand coated at 200°C were higher, averaging 0.00017 mmole Se(IV) / mg Fe and 0.00013 mmole Se(VI) / mg Fe (Figs. 9 and 11). These differences were supposedly caused by the various forms of iron oxide on the IOCS surface. Based on studies by Lo *et al.* [10], high $pH_{(coating)}$ and high $temp_{(coating)}$ favor the formation of crystalline geothite and hematite. The opposite conditions would favor the formation of ferrihydrite. Many studies have pointed out that ferrihydrite, an iron oxide in soil, has better ion adsorption capacity than the crystalline iron oxides, which means that IOCS produced at low $temp_{(coating)}$ has better adsorption capacity for Se(IV) and Se(VI).

Effect of Anions on Se-adsorption

When only Se(IV) and Se(VI) were present in solution, Se(IV) adsorption by various IOCS was not affected by the presence of Se(VI) (Figs. 4 and 5). On the other hand, Se(VI) adsorption by IOCS decreased when Se(IV) was present (Figs. 6 and 7). Therefore, Se(IV) adsorption by IOCS is specific and Se(VI) adsorption is nonspecific.

Figures 6 and 7 illustrate the effects of SO_4^{2-} on Se(VI) adsorption onto IOCS. A solution of 0.0001 M SO_4^{2-} inhibited Se(VI) adsorption on various kinds of IOCS by 10 - 50% while 0.001 M SO_4^{2-} inhibited adsorption by over 90%. Because Se(VI) exists in solution as SeO_4^{2-} whose chemical properties are quite similar to those of SO_4^{2-}, its adsorption onto IOCS was affected by nonspecific adsorption between iron oxides and SO_4^{2-}. Se(IV) adsorption, however was less influenced by SO_4^{2-} (Figs. 4 and 5). With the presence of 0.001 M (96 mg/l) SO_4^{2-}, the adsorption densities of iron oxides for Se(IV) was reduced by 20% maximum indicating that Se(IV) was easily adsorbed by iron oxides and that adsorption was not relatively affected by anions.

Figures 6 and 7 further show that a high concentration of NO_3^- (0.01 N) exerted less influence on Se(VI) adsorption than a low concentration of SO_4^{2-} (0.001 M). Comparing their effects on adsorption densities, 0.01 N NO_3^- did not change the Se adsorption density of IOCS as much as 0.001 M SO_4^{2-} did. In other words, NO_3^- is less competitive than SO_4^{2-} for Se(VI) adsorption sites on the IOCS surface.

Adsorption/Desorption Kinetic Tests

To further understand the adsorption properties of IOCS for Se(VI) and Se(IV), the IOCS which had the best Se-adsorption efficiency was for adsorption/desorption kinetic experiments and adsorption isotherm studies. The IOCS chosen was produced at $pH_{(coating)}=1.0$ and $temp_{(coating)}=105°C$.

The purpose of the kinetic tests was to find the time needed for adsorption or desorption to reach equilibrium. Figures 12 and 13 display the adsorption kinetic test results of Se(VI) and Se(IV), respectively, at different background ionic strengths. After adding Se(VI) or Se(IV) to IOCS suspensions, the residual concentration in the aqueous phase dropped immediately and decreased gradually with time. Similar results of this two-step adsorption process, a rapid step followed by a much slower second step, have been reported for several metal/oxide systems [2, 13, 14]. Pseudo-equilibrium of Se(IV) adsorption was attained within 10 minutes while equilibrium of Se(VI) adsorption required 1.5 hours. Another adsorption kinetic test was performed using a solution of 100 mg/l Se(IV). The results showed that the IOCS adsorbed 100% Se(IV) and that equilibrium was reached within one hour even though the concentration was 10 times that of the previous experiment (Fig. 13). The residual concentrations of Se(IV) and Se(VI) were not significantly changed between 3 hrs to 36 hrs, so a 3-hr reaction time was chosen for the adsorption isotherm experiments to ensure completion of the adsorption process.

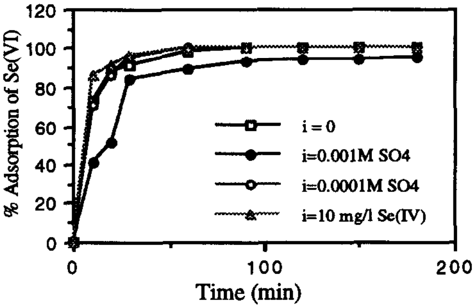

Fig. 12. Results of Se(VI) adsorption kinetic tests (C_0=10 mg/l, pH 6.5)

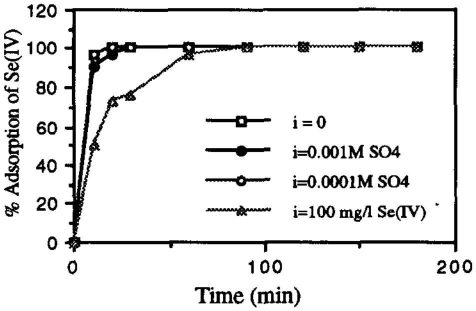

Fig. 13. Results of Se(IV) adsorption kinetic tests (C_0=10 mg/l or 100 mg/l, pH 6.5)

By increasing OH^- concentration, hydroxylation of iron oxides on the surface of IOCS occurred, the adsorbed anions were released, and the IOCS was regenerated. Two concentrations of alkaline solution, 0.01 N and 0.1 N NaOH, were used in the Se-desorption kinetic experiments. The results of Se(VI) desorption are shown in Figs. 14 and 15. Higher concentrations of NaOH solution increased the desorption rate of Se(VI) but could not increase its total desorbed quantity. The differences between the adsorption and desorption efficiencies may have resulted from a delayed desorption process or other irreversible processes.

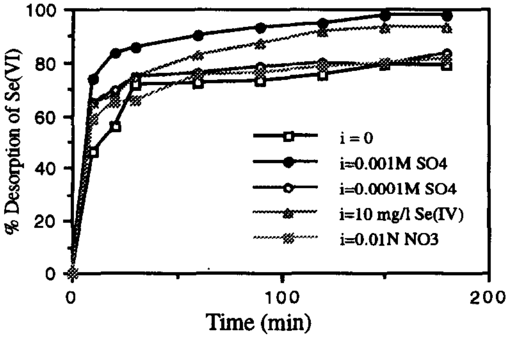

Fig. 14. Results of Se(VI) desorption kinetic tests (C_0=10 mg/l, 0.01 N NaOH)

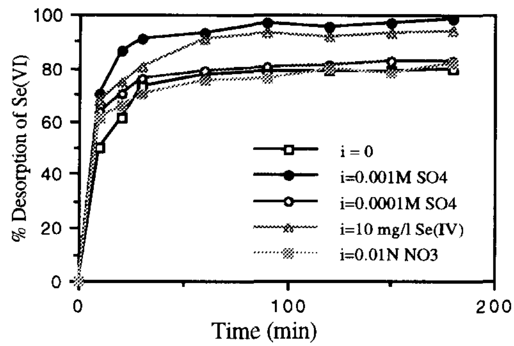

Fig. 15. Results of Se(VI) desorption kinetic tests (C_0=10 mg/l, 0.1 N NaOH)

Adsorption Isotherms

The pH of the adsorption isotherm tests were 4.0 and 6.5. The results (Figs. 16 and 17) show that the lower the pH of solution is, since the lower pH causes the iron oxide surface to carry more positive charges, the higher the amount of Se adsorbed. The amount of Se(IV) adsorbed from pH 4.0 to 6.5 was 0.014 - 0.017 mmole Se / g sand and for Se(VI) was 0.013 - 0.014 mmole Se / g sand. The Langmuir adsorption isotherm was used to fit the experimental data

$$X/M = a\,b\,C_e/(1 + a\,C_e)$$

where, X/M is the quantity of Se adsorbed per unit weight of IOCS (mmole Se / g sand), C_e is the equilibrium concentration of Se in the liquid phase, a is a constant, and b is the maximum value of X/M in the Langmuir model (mmole Se / g sand). Table 1 shows the linear regression results of the Langmuir isotherm.

Table 1. Effect of solution pH on Langmuir isotherms.

Species	Solution pH	a	b	r^2
Se(IV)	4.0	0.6652	0.0167	0.41
Se(IV)	6.5	1.7001	0.0146	0.72
Se(VI)	4.0	1.7378	0.0138	0.31
Se(VI)	6.5	0.2352	0.0140	0.62

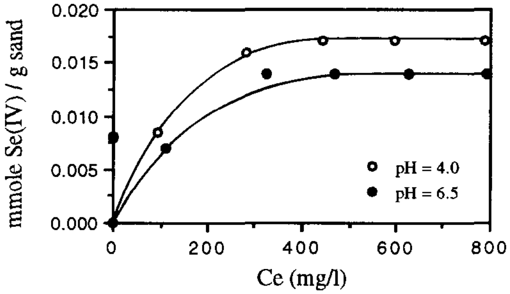

Fig. 16. Adsorption isotherms of Se(IV) (pH$_{(coating)}$=1.0, temp$_{(coating)}$=105°C)

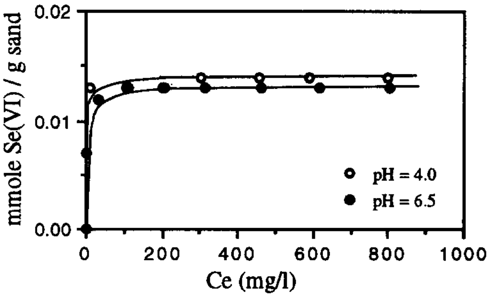

Fig. 17. Adsorption isotherms of Se(VI) ($pH_{(coating)}$=1.0, $temp_{(coating)}$=105°C)

CONCLUSION

The amount of iron coated onto quartz sand was about 4 - 10 mg-Fe / g-sand in this study. The $pH_{(coating)}$ played a very important role in the coating process and in Se removal. A larger quantity of iron was coated onto quartz sand in the lower pH range (0.5 - 2.0), but a greater amount of iron was dissolved from coatings produced at higher $pH_{(coating)}$. The IOCS produced at higher $temp_{(coating)}$ showed more resistance to acid/base than did IOCS formed at lower $temp_{(coating)}$. The IOCS produced at lower $pH_{(coating)}$ and coated at 105°C had better Se(IV) and Se(VI) adsorption efficiencies and higher adsorption densities. Kinetic experiments showed that 3 hrs was enough time for Se adsorption and desorption to reach pseudo-equilibrium. The differences between the adsorption and desorption efficiencies may result from a delayed desorption process or other irreversible processes. Moreover, the Langmuir equation fit the experimental data and showed that the adsorption capacity of IOCS for Se(IV) was 0.014 - 0.017 mmole Se / g sand and for Se(VI) was 0.013 - 0.014 mmole Se / g sand.

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