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Removal of Selenium(VI) from Aqueous Solution with Polyamine-type Weakly Basic Ion Exchange Resin

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Removal of Selenium(VI) from Aqueous Solution with Polyamine-type Weakly Basic Ion Exchange Resin

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Abstract: The adsorption of selenium(VI) on the polyamine-type weakly basic ion exchange resin (Eporasu K-6) was studied by batch and column methods, for developing a process to remove selenium(VI) from waste water. Selenate ion (SeO_4^{2-}) was very strongly adsorbed on the resin over a wide pH range 3 to 12. The adsorption of SeO_4^{2-} on the resin followed a Langmuir type isotherm, and the saturation capacity and Langmuir constant were 1.7 mmol/g and 1.2×10^4 $cm^3/mmol$, respectively. As a rise in concentration of sulfate ion (SO_4^{2-}) in solution significantly reduced an adsorption ability for $SeO_4^{2-} \cdot SeO_4^{2-}$ in waste water must be removed by precipitating first as $CaSO_4 \cdot 2H_2O$ and then as very insoluble $BaSO_4$ prior to use of the resin for removing SeO_4^{2-}. Selenium(VI) adsorbed can easily be eluted from the resin with small volumes of 1 M HCl solution and the resin can be used repeatedly. The adsorption technique with the resin may be used for the final removal of selenium(VI) below the level of the limit of the industrial waste water regulation (0.1 mg/L) in the combination process based on the barium selenate precipitation technique.

Keywords: Removal, selenium(VI), ion exchange

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INTRODUCTION

Selenium is a significant component in ores such as chalcopyrite, galena, and pyrite. In metallurgical processes for copper production, the majority of selenium is concentrated in the anode slime formed during electrolytic refining of copper, but significant quantities are also contained in the sludge accumulating in sulfuric acid plants and in the electrostatic precipitator dust collected during the processing of ores and concentrates. The anode slime containing large amounts of selenium has been processed for recovering valuable metals such as gold, silver, and copper by hydrometallugical processings. In the process liquor and the scrubbing waste water generated in the process for recovering selenium from the anode slime, a fairly high concentration of selenium is often contained. Selenium is also contained in the effluents from the absorption tower for desulfurization in many kinds of industries of glass, rectifier and photo conductor of duplicator etc., and in the waste water from a fire of coal cinders treatment at a coal fired power station. In Japan, selenium has been classified as one of the toxic pollutants since 1994. A great deal of effort to polish technology to treat the selenium-containing process liquors and waste waters in an environmentally acceptable manner is an increasing requisite for advances in these industries.

Selenium is stable in aqueous solution as oxioanions of selenium(IV) and selenium(VI). Four detailed reviews of the works on the removal of both anions from waste water were published by Koren et al. 1992 (1), Kapoor et al. 1995 (2), Mirza and Ramachandran 1996 (3), and Hata et al. 1996 (4) where most works cited deal with precipitation, coprecipitation, adsorption, ion exchange, reverse osmosis elimination, chemical reduction, and biological reduction of selenium entities. These processes are applicable to the removal of selenium(IV) from waste water, but not very effective to selenium(VI) under moderate conditions. Hydrazine can reduce selenium(VI) to elemental selenium only in the hot and concentrated sulfuric acid solution (5). In 1997, Kikuchi and his coworkers (6) found that selenium(VI) is reduced by formic acid with assistance of TiO_2 photo-catalytic action in the weakly acid solution, but this process which involves the formation of a poison gas, hydrogen selenide, is unsuitable for treating waste water on a large scale. Although some anaerobic bacteria are capable of reducing selenium(VI) to elemental selenium (7–11), it is a weak point to require days rather than minutes for the reduction. The barium selenate precipitation process and reduction process with ferrous hydroxide (12, 13) have been promising candidates for removing selenium(VI) from the neutral solution. The process by barium selenate precipitation can be used for separating selenium(VI) from process liquors containing a large quantity of selenium(VI) but is not capable of removing selenium(VI) to a lower concentration than the limit of the industrial waste water regulation (0.1 mg/L). Then this method requires further removal operation of selenium(VI) for disposal to environment (14). By the ferrous hydroxide process, selenium(VI) can be effectively reduced to elemental selenium only at very strict conditions, that is, in a very narrow pH range of around 9 at around 70°C under an inert atmosphere (14). All the above mentioned processes still have some disadvantage in practice.

In this work, the variables of the process of the polyamine-type weakly basic ion exchange resin (Eporasu K-6) developed for adsorbing chromium(VI) from waste water have been evaluated as a unit operation in removing selenium(VI) in waste water after precipitating hardly soluble barium selenate.

EXPERIMENTAL

Materials

Chelating resin (Eporasu K-6) developed by Miyoshi Oil and Fat Company for adsorbing chromium(VI) was used here. The resin is a polyamine-type weakly basic ion exchange resin prepared from styren-divinylbenzen copolymer beads immobilizer (15), but details of the chemical structure have not been published.

Stock solutions of selenium(IV) and selenium(VI) of 1.0 g/L were prepared by dissolving a weighted quantity of analytical reagent grade Na_2SeO_3 and Na_2SeO_4, respectively, in distilled water.

Experimental Procedure

Adsorption capacity for selenium entities was measured by batch and column methods. In the batch method, 500 mL of selenium solution (Se = 30–240 mg/L) was charged in a three-necked flask of 1 L capacity immersed in a thermostated water bath and kept at 25°C. After adjusting the solution pH at the desired value with HCl and NaOH solutions, 0.27 g of the resin dried in vacuum was charged in the solution and agitated with a glass impeller for three hours to allow equilibrium between the solid and liquid phases to be attained. The solution pH was maintained constant at the set value by consuming hydroxyl ion liberated during the ion exchange reaction with drops of 0.01 M HCl solution using an auto-burette. The solutions with suspension of resin were then filtered and the filtrates were analysed for selenium by inductively coupled plasma atomic emission spectroscopy (ICP), and the amounts of selenium adsorbed by the resin were calculated.

In the column method, the selenium(VI) solution (Se(VI) = 10–60 mg/L, pH = 6.0) was passed through the resin bed (7.6 mm $\phi \times 110$ mm) packed in the column at a given space velocity. The effluent was collected in 10 mL fractions. Selenium in the effluents was determined mainly by the 3,3′-Diaminobenzidine (DAB) colorimetric method (16) after reducing selenium(VI) to selenium(IV) with hydrochloric acid in a boiled water bath, but at concentrations higher than 1 mg/L in the filtrate, the ICP method was used.

RESULTS AND DISCUSSION

Adsorption of Se in Batch Experiments

The adsorption capacity of weakly basic ion exchange resin is generally affected by hydroxyl ion in solution. The adsorption capacity of the resin (Eporasu K-6) was determined as a function of pH for selenium(IV) and selenium(VI) by batch experiments, and are shown in Figs. 1 and 2, respectively. Here, the selenium concentration in the starting solution was 60 mg/L. In both figures, the predominant species of selenium(IV) and selenium(VI) are also presented as a function of pH. The amount of selenium(IV) adsorbed by the resin increases as pH increases and has a maximum value of 36 g/L-R at pH of around 10 where selenite ion (SeO_3^{2-}) exists as a stable species. The amount of selenium(VI) adsorbed by the resin jumps up as soon as a stable species in solution changes from $HSeO_4^-$ to SeO_4^{2-} by a rise in pH and has a high value of 46 g/L-R over a wide pH range of 3 to 12. This value approximately in equivalence to the maximum amount of chromium(VI) adsorbed (52 g/L-R) (17) indicates that SeO_4^{2-} has a strong affinity for the resin at the same level as CrO_4^{2-}. At pH 13 a decrease in adsorption is observed. This may be attributed to the depression of ionization of the functional group of the resin due to a large amount of hydroxyl ion in solution. From these results, it is noted that selenium(VI) can be more effectively absorbed on the resin over a wide pH range than selenium(IV). Also as selenium(IV) can be removed from waste water to a level as low as 0.1 mg/L by the existing techniques, the subsequent experiments were carried out only for selenium(VI).

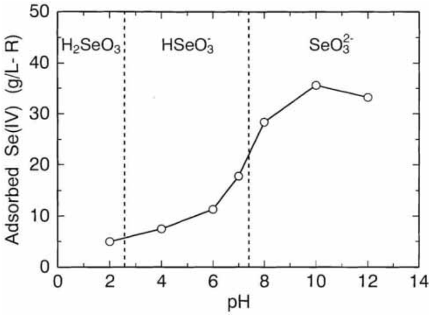

Figure 1. Effect of pH on adsorption of selenium(IV) on resin.

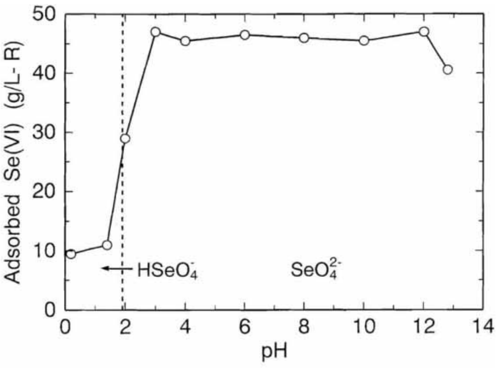

Figure 2. Effect of pH on adsorption of selenium(VI) on resin.

Figure 3 shows a Langmuir type of adsorption isotherm obtained from the experiments setting the charge of resin at 0.27 g and varying the selenium(VI) concentration from 30 mg/L to 240 mg/L at pH 6.0 and 25°C. In this figure, Q_{eq} and C_{eq}, denote an equilibrium adsorption capacity of the resin for selenium(VI) (mmol/g) and an equilibrium concentration of selenium(VI) in solution, respectively. Taking into account Q_{max} and K for a saturation adsorption capacity (mmol/g) and a Langmuir constant (cm^3/mmol), the Langmuir adsorption isotherm is expressed by Eq. (1),

$$Q_{eq} = KQ_{max}C_{eq}/(1 + KC_{eq}) \tag{1}$$

Rearranging Eq. (1) yields:

$$C_{eq}/Q_{eq} = (1/Q_{max})C_{eq} + 1/KQ_{max} \tag{2}$$

By plotting C_{eq}/Q_{eq} versus C_{eq}, the slope is $1/Q_{max}$ and the intercept is $1/KQ_{max}$. As shown in Fig. 3, a plot gives a straight line, which indicates

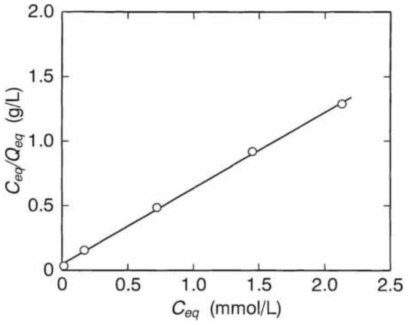

Figure 3. Langmuir plot for adsorption of selenum(VI) on resin.

that only a monolayer is formed in adsorption of selenium(VI) on the resin. The slope and intercept give the values of 0.585 g/mmol and 0.048 g/L, respectively. From these values, the saturation capacity and Langmuir constant were calculated to be 1.7 mmol/g and 1.2×10^4 cm^3/mmol, respectively.

Waste waters often contain significant quantities of various anions such as SO_4^{2-} and Cl^-. Specially, as SO_4^{2-} has chemical similarity to SeO_4^{2-}, a competitive adsorption reaction may take place between SeO_4^{2-} and SO_4^{2-}. The influence of SO_4^{2-} and Cl^- on the adsorption of selenium(VI) on the resin was determined by adding various amounts of Na_2SO_4 or NaCl to the selenium(VI) solution of 60 mg/L at pH 6.0, and is shown in Fig. 4. In the coexistence of SO_4^{2-}, the amount of selenium(VI) adsorbed on the resin starts to decrease from SO_4^{2-}/SeO_4^{2-} mole ratio of 0.3 and shows a decrease of 50 percent at mole ratio of 2. In the coexistence of Cl^-, the amount of selenium(VI) adsorbed starts to decrease at Cl^-/SeO_4^{2-} mole ratio of 3 and shows a decrease of 50 percent at mole ratio of 20. These indicate that the adsorption of the resin is in order of $SeO_4^{2-} > SO_4^{2-} \gg Cl^-$, but SO_4^{2-} in waste water must be removed prior to use of the resin for removing SeO_4^{2-} because of competitive adsorption.

In an aqueous solution, barium ion reacts with selenate ion to form barium selenate ($BaSeO_4$) over a wider pH range. As reported in the previous publication (14), an increase in $BaCl_2$/Se(VI) mole ratio in the starting solution of 780 mg Se(VI)/L led to a drastic decrease in concentration of selenium(VI) and a terminal concentration of selenium(VI) leveled off around 2 mg/L at $BaCl_2$/Se(VI) mole ratio above 2.5. This value was still above the limit of the industrial waste water regulation (0.1 mg/L) against selenium. In the use of the polyamine-type weakly basic ion exchange resin for the final removal of selenium(VI) in combination with a process based on the barium selenate precipitation, there is no problem caused by SO_4^{2-}, because most of SO_4^{2-} has been removed

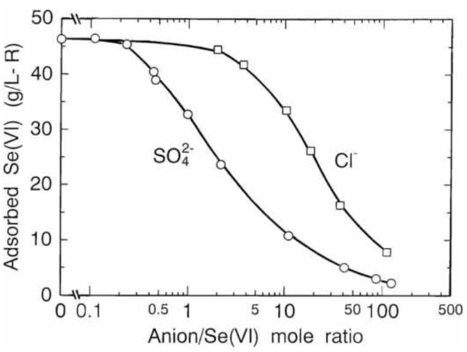

Figure 4. Effect of coexisting anion on adsorption of selenium(VI) on resin.

as insoluble $BaSO_4$. But barium ion remains in the solution together with SeO_4^{2-}. Figure 5 shows a plot of the residual concentration of selenium(VI) versus the residual concentration of barium in the solution after adsorption of selenium(VI) by the resin at pH 6.0. Here, the selenium(VI) concentration in the starting solution was 60 mg/L which was in excess to loading the resin up to the adsorption capacity. The residual concentration of selenium(VI) stays unchanged at 14 mg/L in the presence of barium ion up to the concentration of about 1400 mg/L. The further increase in barium resulted in a drastic decrease in selenium(VI) concentration down to a terminal value of around 2 mg/L which is exactly equal to the terminal concentration observed in the removal of selenium(VI) as $BaSeO_4$ by adding a large excess of $BaCl_2$. This reveals that the presence of barium ion in solution brought about no influence on the adsorption capacity for selenium(VI). At a high barium concentration, in addition to the adsorption by the resin selenium(VI) is furthermore removed to a low level by formation of $BaSeO_4$. The $BaSeO_4$ formed in the presence of larger quantities of barium ion may be in suspension in the resin bed or cover the surface of the resin and results in affecting negatively ion-exchange activity. Therefore, a level of barium in the solution coming from the $BaSeO_4$ processing should be hold below 1 g/L to prevent the formation of $BaSeO_4$ in the resin adsorption process.

Adsorption of Se(VI) in Column Experiments

As described above, the resin of the type under consideration gives a hope of effective adsorption of selenium(VI) over a wider pH range. In order to evaluate the adsorption process as a unit process for removal of selenium(VI) from waste water, the adsorption and elution characteristics of selenium(VI) were studied by column experiments.

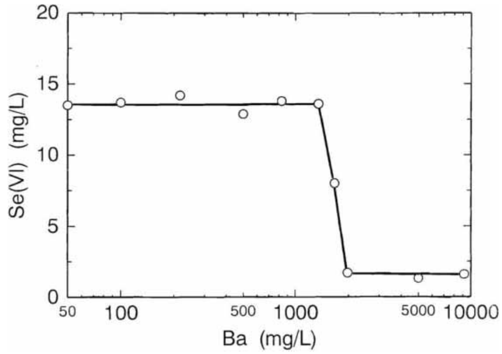

Figure 5. Effect of barium ion on adsorption of selenium(VI) on resin.

In the column method, the space velocity which depends on sort, concentration, and chemical entity of metal ions is one of the important factors affecting the adsorption efficiency of the resin. The selenium(VI) solution of 10 mg/L (pH = 6.0) was passed through the resin bed (7.6 mm $\phi \times 110$ mm) packed in the column at space velocities of 10 and 50. The breakthrough curves for selenium(VI) on the resin are shown in Fig. 6. In this figure, <0.02 mg/L denotes the detectable limit of selenium(VI) by the DAB colorimetric method. The point where the resin was saturated with selenium(VI) is indicated by • symbol. At both space velocities, selenium(VI) starts to be detected from the effluent volume of 12 L but then leaks out in inverse parabolic for SV of 10, while in parabolic for SV of 50. Consequently, the permissible effluent volume for disposal when Se(VI) leakage reached the level of 0.1 mg/L is 19.5 L for SV of 10, while reduces to 14.6 L for SV of 50. The amount of selenium(IV) adsorbed by the resin at pH = 6.0 was found to be 46.5 g/L-R (Fig. 2). This value gives 23.3 L as an effluent volume (when the resin becomes saturated for selenium(VI) concentration of 10 mg/L in the feed solution), which is in fair agreement with the value of 23.5 L shown by the breakthrough curve.

The selenium(VI) concentration of feed solution is also an important factor affecting the adsorption efficiency of the resin. The breakthrough curves are shown for selenium(VI) concentrations of 10, 25 and 60 mg/L in the feed solution at a space velocity of 10 in Fig. 7. After selenium(VI) starts to be detected in the effluent, the selenium(VI) concentration in the effluent leaked out curves gently up with an increase in the effluent volume at selenium(VI) concentration of 10 mg/L in the feed solution, while it jumps sharply up at both 25 and 60 mg/L. The amount of selenium(VI) adsorbed on the resin calculated from the permissible effluent volume for disposal is 39.1 g/L-R for selenium(VI) concentration of 10 mg/L in the feed solution, 36.5 g/L-R for 25 mg/L and 32.6 g/L-R for 60 mg/L, which

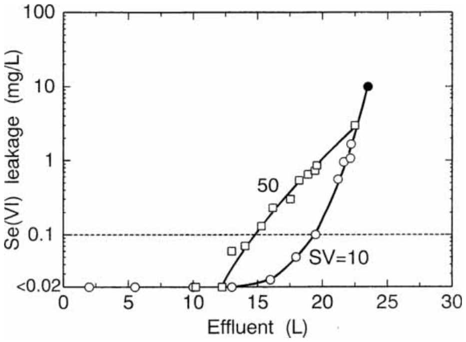

Figure 6. Breakthrough curves of selenium(VI) at different space velocities (Se(VI) = 10 mg/L, pH = 6.0, bed volume of resin = 5.0 mL).

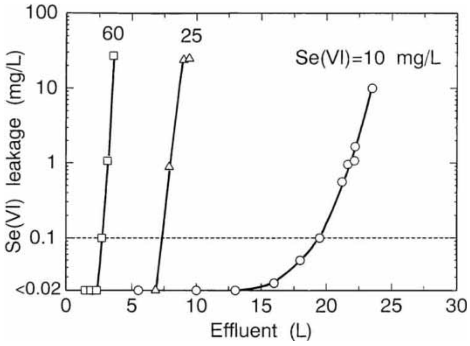

Figure 7. Breakthrough curves of selenium(VI) at different concentrations of selenium(VI) (pH = 6.0, bed volume of resin = 5.0 mL, SV = 10).

indicates that it is not advisable to use the resin for removing a high level of selenium(VI).

From Fig. 2, the adsorption of selenium(VI) is limited to a very low level in strongly acidic or basic solutions. In order to find a suitable eluent of selenium(VI) absorbed, batch experiments were carried out for hydrochloric acid and sodium hydroxide solutions of various concentrations. Here, the resin loaded by selenium(VI) at 46 g/L-R was contacted with the eluents for three hours. As shown in Fig. 8, in hydrochloric acid solution the amount of selenium(VI) adsorbed by the resin decreases sharply to 6 g/L-R with a slight increase in acidity and then still continues to decrease marginally as the acidity increases. In sodium hydroxide solution, the amount of selenium(VI) adsorbed decreases gradually with an increase in basicity and then stays at around 13 g/L-R over NaOH concentration range above 1.0 mol/L. This suggests that the hydrochloric acid solution will act more effectively as

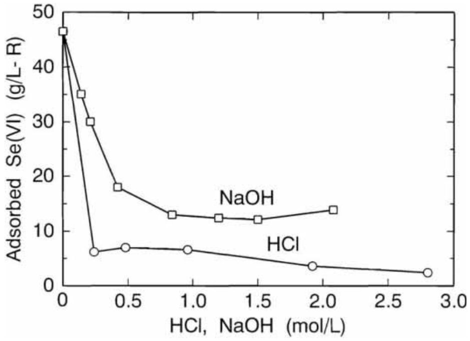

Figure 8. Effect of solution acidity and basicity on adsorption of selenium(VI) on resin.

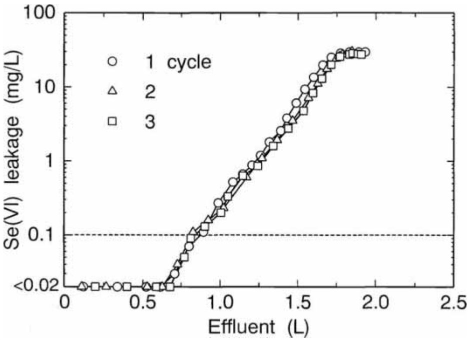

Figure 9. Breakthrough curves of selenium(VI) in recycle test (Se(VI) = 25 mg/L, pH = 6.0, bed volume of resin = 1.0 mL, SV = 10).

an eluent of selenium(VI) from the resin than will the sodium hydroxide solution.

The recycle test for the adsorption and elution of selenium(VI) was performed by column experiment. The selenium(VI) solution of 25 mg/L (pH = 6.0) was fed to the resin bed (7.6 mm $\phi \times$ 22 mm) packed in the column at a space velocity of 10 and selenium in the effluents was analysed. After the selenium concentration in the effluent was reached to concentration in the feed solution, the selenium(VI) solution remaining in the column was removed by passing the distilled water of 100 mL and then 1 M HCl of 40 mL (40 L/L-R) was passed through the resin bed at a space velocity of 10. Selenium in the eluates was analysed. After 1 M HCl eluent was removed from the resin by passing the distilled water of 100 mL, the cycles of adsorption and elution were repeated. The breakthrough curves for selenium(VI) on the resin and elution curves for selenium(VI) from the resin in the recycle test are shown in Figs. 9 and 10, respectively.

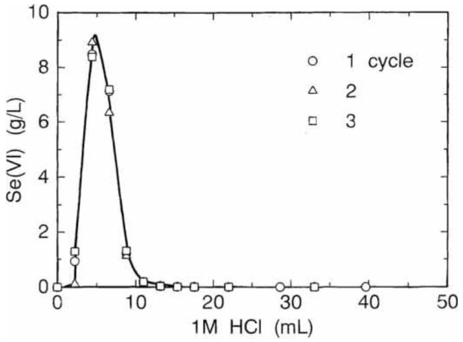

Figure 10. Elution curves of selenium(VI) in recycle test (bed volume of resin = 1.0 mL, SV = 10).

A decrease in loading capacity caused by recycling the resin is not observed and selenium is eluted from the resin with relatively small volumes of 1 M HCl (22 L/L-R), which indicate that the resin can be used repeatedly for the removal of selenium(VI) from waste water.

Process for Removal of Selenium

Selenium is extracted from anode slime generating in the copper electro-refining step. The selenium-bearing waste solutions in conventional processes for anode slime treatment come from selenium-recovery step based on SO_2-reduction in acidic sulfate solution and the gas washing step in oxidation roasting for separation of selenium from the slime. In the previous paper (14), the three-stage process for removal of selenium(IV) and selenium(VI) from such waste water containing sulfuric acid was proposed. In the first stage where ferric sulfate and calcium hydroxide are added, selenium(IV) is precipitated as $Fe_2(SeO_3)_3 \cdot 5H_2O$ (18) and a majority of SO_4^{2-} is also precipitated as $CaSO_4 \cdot 2H_2O$ at pH 3–4. In the second stage, selenium(VI) is removed to a lower concentration than 20 mg/L as $BaSeO_4$ by adding barium chloride at pH 5–6 and also the remaining SO_4^{2-} is precipitated as $BaSO_4$. In the third stage, the remaining selenium(VI) is removed to a lower concentration than 0.1 mg/L by reduction-precipitation of selenium(VI) to elemental selenium with ferrous hydroxide at pH 9 at 70°C in an atmosphere of nitrogen. The third stage process requires very strict conditions to effectively remove selenium(VI).

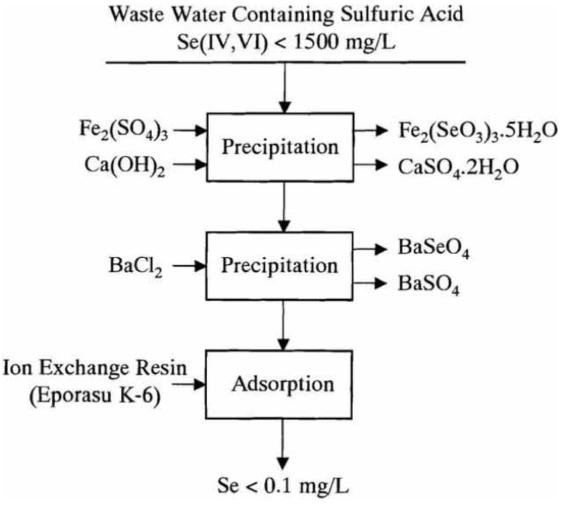

Figure 11. Flowsheet of process for removal of selenium from industrial waste water.

Replacement of the ferrous hydroxide reduction process with the adsorption process using the polyamine-type weakly basic ion exchange resin (Eporasu K-6) yields a simplified selenium removal process which is shown in Fig. 11. This process seems to be promising to remove selenium from high concentration levels of selenium(IV) and selenium(VI) in acidic sulfate waste water to below 0.1 mg/L. Here, the first stage can be omitted for waste water including relatively small amounts of selenium(IV) and selenium(VI).

CONCLUSIONS

In order to develop the process to remove selenium(VI) from waste water the adsorption of selenium(VI) on the polyamine-type weakly basic ion exchange resin (Eporasu K-6) was investigated by batch and column methods.

Selenium(VI) is strongly adsorbed in the form of SeO_4^{2-} on the resin over a wide pH range 3 to 12. The adsorption ability of the resin is $SeO_4^{2-} > SO_4^{2-} \gg Cl^-$ in order, but as SO_4^{2-} reduces fairly the adsorption ability of the resin for selenium(VI), it must be removed from waste water such as by precipitating as very insoluble $BaSO_4$ prior to use of the resin for removing selenium(VI). Adsorbed selenium(VI) can easily be eluted from the resin with small volumes of 1 M HCl solution and the resin can be re-used. The adsorption process using the resin can be combined in a final stage to remove selenium(VI) below the level of the limit of the industrial waste water regulation (0.1 mg/L) in the combination process based on the $BaSeO_4$ technique.

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