

PRELIMINARY STUDY OF MULTIPLE HEAVY METAL REMOVAL USING WASTE IRON OXIDE TAILINGS

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ABSTRACT

This paper described a preliminary study of heavy metal adsorption from aqueous solution on a type of waste iron oxide tailings in batch experiments. The tailings material was derived from a mineral ore processing industry and contained more than 30% iron oxides. The metal ions used in the adsorption experiments included Se(VI), Se(IV), Cr(VI), Cr(III), Pb(II) and Cd(II). Adsorption experiments were conducted in both a single-metal system and a multiple-metal system at different pH values and metal concentrations. The experimental results showed that among the six heavy metals, Pb(II), Cr(III), Cd(II) and Se(IV) could be effectively removed by adsorption on the iron oxide tailings. Under the similar conditions, Se(VI) was barely removed and Cr(VI) removal was small. Thus, only four metal ions, Pb(II), Cr(III), Cd(II) and Se(IV), were further used in the multiple-metal system. It was found that these four metal ions were adsorbed by the tailings material simultaneously to a great extent in an order of $Pb(II) \approx Cr(III) > Se(IV) > Cd(II)$ at pH 6.5 or $Pb(II) \approx Cd(II) > Cr(III) > Se(IV)$ at pH 9. In either a single-metal or a multiple-metal system, the influence of pH (6.5 and 9) on the adsorption of Pb(II) and Cr(III) was negligible. By contrast, the removal of Se(IV) was higher at pH 9 than at pH 6.5, while the removal of Cd(II) followed the opposite trend. The kinetic experiments showed that the rates of Pb(II), Cr(III), Cd(II) and Se(IV) adsorption on the tailings in a multiple-metal system were fast at 20°C and the tested pH (6.5 and 9). Most of the metal adsorption was completed in 5 min. These high adsorption rates were likely attributed to the strong affinity of the metal ions to the iron oxide tailings surface. It can be concluded that due to their low cost and relatively high adsorption rate and capability, this type of waste iron oxide tailings has the potential to be utilized for cost-effective removal of heavy metals from water and wastewater.

INTRODUCTION

The presence of heavy metals in the aquatic environment is of major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy production, battery manufacturing, and paint manufacturing. Since the majority of heavy metals do not degrade into harmless end-products in the aquatic environment, their removal before discharge into receiving waters becomes necessary. Otherwise, they could pose threats to public health or affect the aesthetic quality of potable water.

Treatment processes for heavy metal removal from aqueous solutions include precipitation, membrane filtration, ion exchange, adsorption and co-precipitation /adsorption. Adsorption as one of the most promising techniques for heavy metal removal has received considerable attention, particularly in the cases where suitable low-cost adsorptive materials could be available. Hence, extensive research work has been focused on the exploration of inexpensive adsorbents, especially developed from various industrial waste materials, i.e., fly ash, metal hydroxides, blast furnace slag, red mud, biomass, carbonaceous materials, etc. [1-7]. It is believed that the development and utilization of cost-effective adsorbents is often a critical issue in the development of viable adsorption techniques for heavy metal removal.

A type of waste tailings was derived from a mineral ore processing industry in Canada. Over 1000 tons of these tailings was generated annually and stored in slurry ponds. This tailings material contains significant amounts of iron oxides that could have adsorptive ability for removing some heavy metals and other aquatic pollutants. Therefore, these tailings have the potential to be used as a cost-effective adsorbent for removing various metal ions in wastewater treatment.

The primary objective of this study was to evaluate the feasibility of using this type of waste iron oxide tailings as an adsorbent for removal of heavy metals from aqueous solutions. The heavy metals to be tested in the experiments included Se(VI), Se(IV), Cr(VI), Cr(III), Cd(II) and Pb(II). In the experiments, equilibrium adsorptions using both a single-metal system and a multiple-metal system were examined at different pH values and metal concentrations. The adsorption kinetics in a multiple-metal system was evaluated as well.

MATERIALS AND METHODS

Materials

The iron oxide tailings used in the present experiments were dark brown fine-textured powders, which were produced by drying the tailings slurry at 80°C. The slurry was obtained from the tailings disposal pond [8]. The elemental composition of the dry tailings is shown in Table 1, which was determined by using an inductively coupled plasma-mass spectrometer (ICP-MS). The percentage of oxides was obtained through conversion of the elemental composition by assuming that the elements were present in their highest oxidation state. In addition to the major elements shown in Table 1, the tailings also contained small amounts of other elements (< 0.5%), such as Co, K, Mn, Na, Ti, Zn, etc. The moisture of the dried tailings was 0.5%. The median particle size of the raw tailings was 4.2 µm, measured by laser granulometry. The BET surface area of the dry tailings was 32.8 m²/g, determined with a Micromeritics Accusorb 2010 surface area analyzer. The pH value of the dried tailings was 6.76±0.05 measured by a standard method [9]. The predominant constituent in the tailings was iron, which was probably partially amorphous and partially crystalline. X-ray diffraction (XRD) analysis showed that the majority of crystalline iron oxides in the tailings were magnetite (Fe₃O₄), although most of iron in the original ore was in a form of goethite (α-FeOOH) [8].

Table 1. Major composition of the dry tailings

Constituent	Al	Ca	Cr	Fe	Mg	Ni	S	Si
wt%	1.76	4.12	0.97	23.05	0.89	1.60	1.85	8.70
Oxides	Al ₂ O ₃	CaO	Cr ₂ O ₃	Fe ₂ O ₃	MgO	NiO	SO ₄	SiO ₂
wt%	3.32	5.51	1.41	32.93	1.48	2.03	5.54	18.60

For heavy metal adsorption experiments, the stock solutions of Se(VI), Se(IV), Cr(VI), Cr(III), Cd(II) and Pb(II) (all in 1000 mg/L) were prepared in reverse osmosized and deionized (RO+DI) water by using Na₂SeO₄, Na₂SeO₃, K₂Cr₂O₇, Cr(NO₃)₃·9H₂O, Cd(NO₃)₂·4H₂O and Pb(NO₃)₂, respectively. The working solutions of the metal ions were freshly prepared by diluting the stock solutions with RO+DI water and contained 0.01 M NaNO₃ for adjusting ionic strength. 0.1 - 0.5 N HNO₃ and NaOH were used for adjusting the pH values of the working solutions.

Experimental methods

Adsorption of heavy metals by the tailings powders was examined in two types of batch experiments, using single-metal solutions and multiple-metal solutions. Each single-metal solution contained one of Se(VI), Se(IV), Cr(VI), Cr(III), Cd(II) and Pb(II), while each multiple-metal solution contained all of Se(IV), Cr(III), Cd(II) and Pb(II). The use of multiple metal solutions was to simulate competitive adsorption between metals for the adsorption sites because metal-bearing wastes commonly contained a range of heavy metals. In the batch experiments, approximately 200 mg of the tailings powders and 100 mL of 1 - 10 mg/L metal solution was initially added in a 250-mL Erlenmeyer flask. The flask was capped and placed on a shaker at room temperature (about 20°C) and 180 rpm for 24 h to ensure approaching equilibrium. Two pH values (6.5 and 9.0) were used in the experiments. Experimental pH was manually maintained at the defined value with 0.1 – 0.5 N HNO₃ and NaOH at intervals of every 1 – 2 hours. After 24 h of the reaction period, all samples were filtered by a 0.45-µm membrane filter, acidified to pH < 2 with HNO₃, and stored at 4°C prior to analyses. The metal concentrations in the sample solutions were determined by using ICP-MS. The quantity of adsorbed metals in each sample was calculated by the difference of the initial and final amounts of metals in the solution divided by the weight of the added tailings.

The experiments for determining multiple-metal adsorption kinetics were conducted at 20±1°C and two pH (6.5 and 9.0). Before the start of each kinetic run, approximately 1000 mg of the tailings was weighed and loaded in a 1-L two-neck flask that was placed on a water bath with magnetically stirring. Five hundred mL of aqueous solution containing 50 mg/L of each metal (Se(IV), Cr(III), Cd(II) and Pb(II)) and 0.01 M NaNO₃ was added into the flask. This was correspondent to an initial load of four selected metals in 25 mg each metal/g tailings. After the start of the experiment, several milliliters of the reaction solution were sampled with an air displacement pipettor at the different time up to 24 hr. The sampled solution was immediately filtered using a 0.45-µm membrane filter and analyzed by ICP-MS

for metal concentrations. The pH of the reaction solution was maintained well constant during the kinetic tests.

To determine the amount of metals released from the raw tailings material, two blank experiments were conducted at pH 6.2 and 9.0, following the same procedure but using water without metal ions. The quantity of five metals (Se, Cr, Cd, Pb and Fe) leached from the blank experiments is shown in Table 2. Clearly, the leached metals from the waste iron oxide tailings are negligible and thus are excluded in the later adsorption calculations.

Table 2. Leached metals from the waste tailings in the blank experiments.

Run No.	pH	Se, $\mu\text{g/g}$	Cr, $\mu\text{g/g}$	Cd, $\mu\text{g/g}$	Pb, $\mu\text{g/g}$	Fe, $\mu\text{g/g}$
Blank-1	6.2	0.1	1.5	0.1	0.2	6.4
Blank-2	9.0	0.6	26.5	0.01	0.02	1.3

RESULTS AND DISCUSSION

Adsorption of a single metal

Adsorption of a single metal was examined at pH 6.5 and 9.0 using 10 mg/L of Se(VI), Se(IV), Cr(III), Cd(II), and Pb(II), and 20 mg/L of Cr(VI), respectively. The experimental results are shown in Figure 1. It can be seen that the removal of Se(VI) is extremely low at both pH values. This is in agreement with the literature results that iron oxide was not able to adsorb Se(VI) [10] and that iron co-precipitation was not efficient to remove Se(VI) from water [11]. In contrast, the removal of Se(IV) was much higher than that of Se(VI). Similarly, the removal of Cr(III) was much higher than that of Cr(VI). The pH more significantly affected adsorption of Se(VI), Se(IV) and Cr(VI), which were all negatively charged species in water (as SeO_4^{2-} , SeO_3^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$). The lower the pH, the better the removal of these metal anions. This was attributed to the fact that the higher pH causes the iron oxide surface to carry more negative charges and would tend more significantly to repulse the negatively charged species in solution.

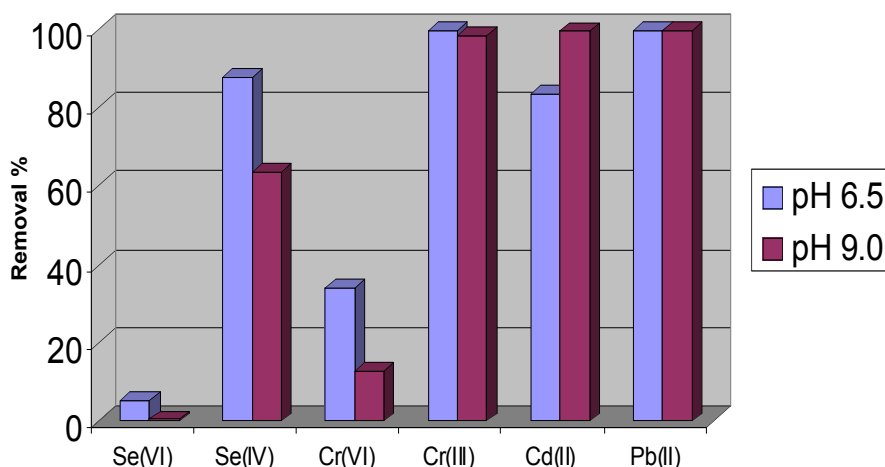


Figure 1. Removal of single metal ion by batch adsorption on the waste tailings.

Under the same conditions, the removal of Cd(II) was higher at pH 9 than at pH 6.5, while Pb(II) was almost completely removed at both pH values. Basically, the adsorption of Pb(II), Cr(III) and Cd(II) (at pH 9) by the tailings powders was more efficient. The pH had less influence on the adsorption of Pb(II) and Cr(III). The general orders of the metal removal determined in these single-metal adsorption experiments are as:

Pb(II) \approx Cr(III) > Se(IV) > Cd(II) > Cr(VI) > Se(VI) (at pH 6.5), and

Pb(II) \approx Cd(II) > Cr(III) > Se(IV) > Cr(VI) > Se(VI) (at pH 9.0).

Adsorption of multiple metals

Based on the results from the experiments for the single-metal adsorption, only Se(IV), Cr(III), Cd(II) and Pb(II) were selected for the multiple-metal adsorption experiments. The experiments were conducted at three metal concentrations (1, 5, and 10 mg/L for each metal) and two pH levels (6.5 and 9.0). The results are shown in Figures 2 to 5. Generally, the four tested metal ions were removed simultaneously to a great extent and the adsorption capacities of these four metal ions were all significantly increased with their equilibrium concentrations. The experimental pH had very little influence on Pb(II) adsorption with an extremely low Pb(II) residual concentration (0.1 - 4 $\mu\text{g/L}$); while it had only a little influence on Cr(III) adsorption, although the residual Cr(III) concentration (7 - 111 $\mu\text{g/L}$) was slightly higher at the higher pH. By contrast, the pH affected the adsorption of Se(IV) and Cd(II) more significantly. The removal of Se(IV) at pH 9.0 was lower than that at pH 6.5; while the removal of Cd(II) followed the opposite trend. Therefore, the residual Se(IV) concentration at pH 9.0 and the residual Cd(II) concentration at pH 6.5 were significantly higher. At the highest initial metal concentration (10 mg/L for each metal), the removal efficiency was 99.98% for Pb(II), 99.94% for Cr(III), 81.07% for Cd(II), and 97.14% for Se(IV) at pH 6.5; and it was 99.96% for Pb(II), 98.89% for Cr(III), 99.72% for Cd(II), and 84.43% for Se(IV) at pH 9.0. The general removal orders determined in these adsorption experiments of the multiple metal ions are virtually similar to those observed in the single-metal adsorption

system as: $Pb(II) \approx Cr(III) > Se(IV) > Cd(II)$ (at pH 6.5), and $Pb(II) \approx Cd(II) > Cr(III) > Se(IV)$ (at pH 9.0).

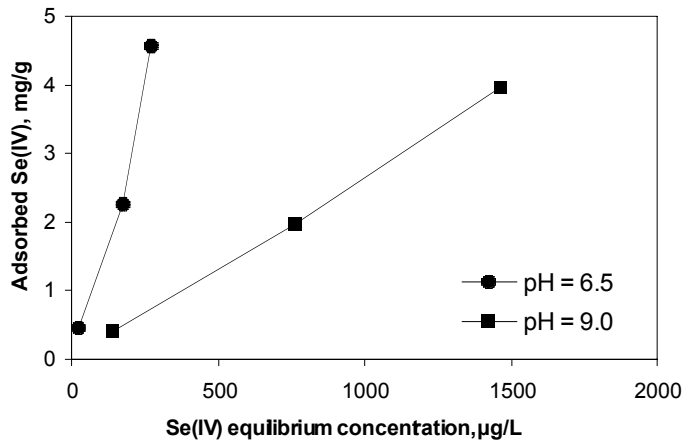


Figure 2. Removal of Se(IV) in a multiple-metal system.

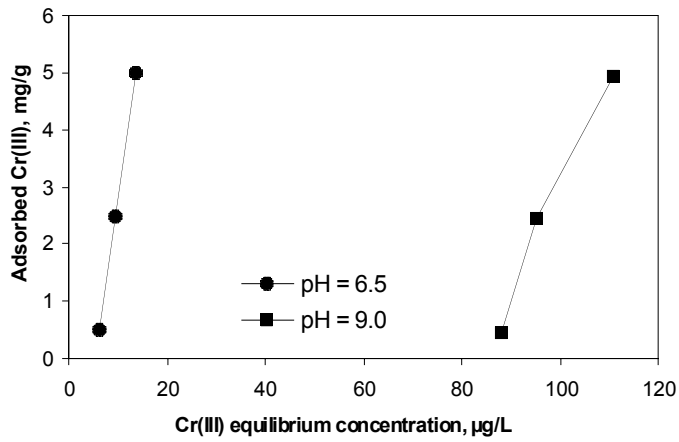


Figure 3. Removal of Cr(III) in a multiple-metal system.

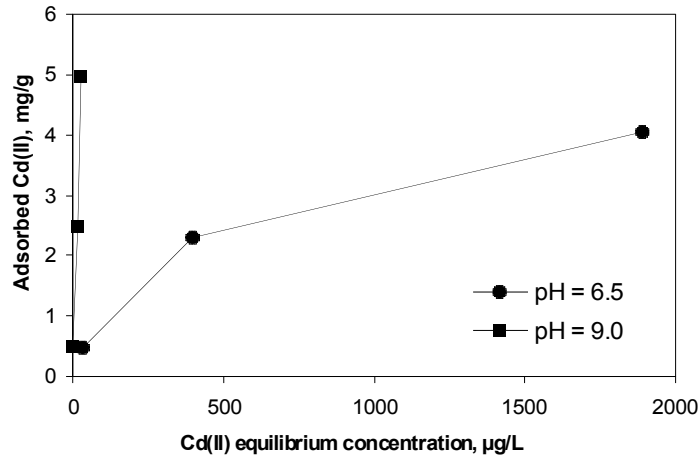


Figure 4. Removal of Cd(II) in a multiple-metal system.

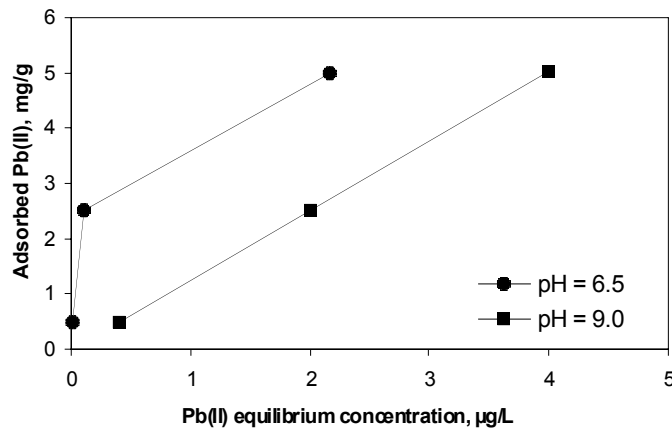


Figure 5. Removal of Pb(II) in a multiple-metal system.

Comparison of single and multiple metal adsorptions

The results of the single-metal adsorption were compared with those of the multiple-metal adsorption at a similar initial metal concentration (10 mg/L) as shown in Figures 6 and 7 for pH 6.5 and 9.0, respectively. It can be seen that the behavior of removing Pb(II), Cr(III) and Cd(II) was almost identical for the single-metal and multiple-metal systems except for Cd(II) at pH 6.5. This implied that adsorptions of these three metal ions on the iron oxide tailings were barely competitive, or that the iron oxide tailings had a large amount of surface sites for metal adsorption. These metals might be adsorbed on the different active surface sites. However, the adsorption of Se(IV) from the multiple-metal system was slightly larger than that from the single-metal system. It is presumably because the anion repulsion force that would play an important role in the adsorption of the negatively charged Se(IV) was reduced after the positively charged Pb(II), Cr(III) and Cd(II) were adsorbed on the surface of the iron oxide tailings.

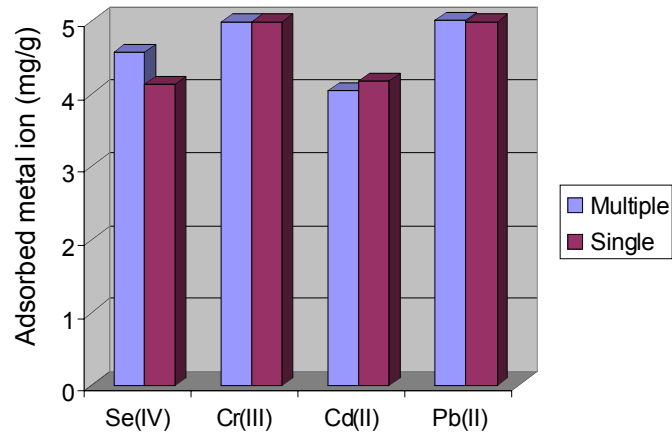


Figure 6. Comparison of single and multiple metal adsorptions at pH 6.5 with an initial concentration of 10 mg/L for each metal.

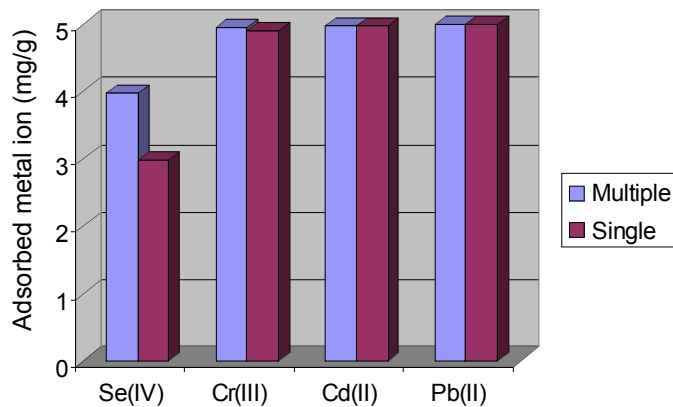


Figure 7. Comparison of single and multiple metal adsorptions at pH 9.0 with an initial concentration of 10 mg/L for each metal.

Adsorption kinetics in a multiple-metal system

The adsorption kinetic data for 3 h are shown in Figures 8 and 9 for pH 6.5 and pH 9.0, respectively. The actual initial concentrations of metal ions were 48.5 mg Se(IV)/L, 51.1 mg Cr(III)/L, 49.8 mg Cd(II)/L, and 51.7 mg Pb(II)/L. It can be seen that most of the metal adsorption on the tailings was completed in 5 min at both tested pH. Therefore, kinetic curves were nearly flat after 5 min. These high adsorption rates were likely attributed to the strong affinity of those metal ions to the iron oxide tailings surface. The removal percentage at the first 5 min is 99.99% Pb(II), 99.90% Cr(III), 99.21% Se(IV) and 95.11% Cd(II) at pH 6.5, and 99.99% Pb(II), 99.98% Cd(II), 99.97% Cr(III), and 90.20% Se(IV) at pH 9.0. The orders of the removal capacities obtained from these kinetic experiments are similar to those described before for the multiple-metal adsorption. It was also observed that Cd(II) was

desorbed after 10-min in the experiment at pH 6.5 (Figure 8), but no explanation could be provided for this phenomena.

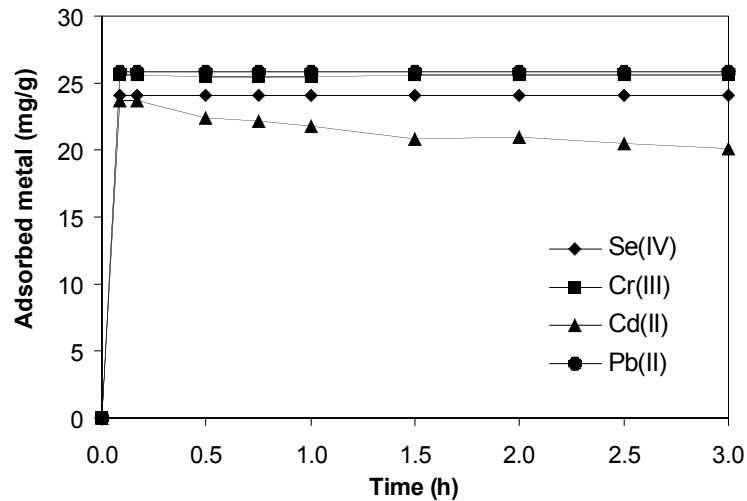


Figure 8. Kinetic data of multiple-metal adsorption on the tailings at 20°C and pH 6.5.

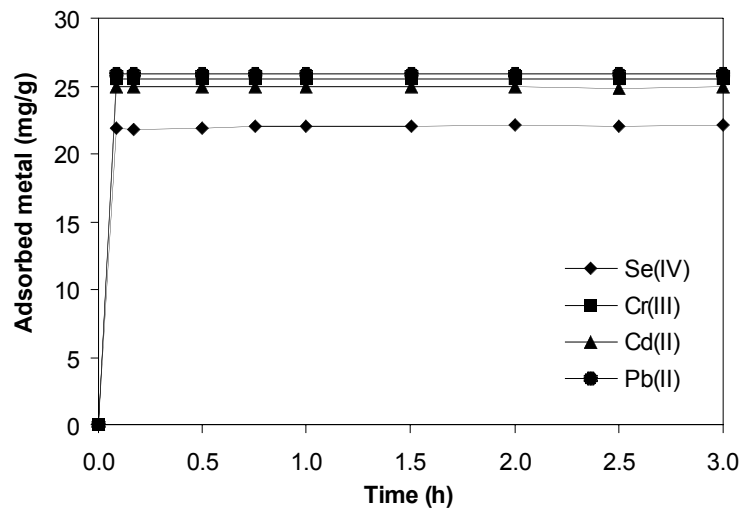


Figure 9. Kinetic data of multiple-metal adsorption on the tailings at 20°C and pH 9.0.

Potential utilizations of waste iron oxide tailings

Due to their low cost, relatively high adsorption rate and high removal capability, the waste iron oxide tailings can be utilized for removal of Pb(II), Cr(III), Cd(II), Se(IV) as well as some other pollutants from wastewater. In particular, the following applications can be considered:

- As adsorbents for sewage treatment to remove heavy metals.

- As adsorbents for removal of heavy metals from landfill leachates.
- As adsorbents to treat heavy metal containing industrial wastewater.

Any of above potential applications should be examined in laboratory tests. Modification and granulation of this tailings material may be needed for individual applications, particularly for the cases that require column adsorption.

CONCLUSIONS

The following conclusions can be drawn from the presented work:

- (1) A type of waste iron oxide tailings was studied in batch adsorption experiments for heavy metal removal from aqueous solution. Six metal ions, Se(VI), Se(IV), Cr(VI), Cr(III), Cd(II) and Pb(II), were included in the tests. It was found that only Pb(II), Cr(III), Cd(II) and Se(IV) could be effectively removed by adsorption on the tailings. Under the similar conditions, Se(VI) was barely removed and Cr(VI) removal was small.
- (2) In a multiple-metal system, the four tested metals Pb(II), Cr(III), Cd(II) and Se(IV) were adsorbed by the tailings material simultaneously to a great extent in an order of $\text{Pb(II)} \approx \text{Cr(III)} > \text{Se(IV)} > \text{Cd(II)}$ at pH 6.5 or $\text{Pb(II)} \approx \text{Cd(II)} > \text{Cr(III)} > \text{Se(IV)}$ at pH 9.0. This order was generally similar to that observed from the single-metal adsorption system.
- (3) In either a single-metal or a multiple-metal system, the influence of pH (6.5 and 9.0) on adsorption of Pb(II) and Cr(III) was negligible. By contrast, the adsorption of Se(IV) at pH 9.0 was higher than that at pH 6.5, while the adsorption of Cd(II) followed the opposite trend.
- (4) Comparison of the metal adsorption in the single-metal and multiple-metal systems suggested that adsorptions of these metals on the iron oxide tailings were barely competitive. They were likely adsorbed on the different active surface sites.
- (5) The kinetic experiments showed that the rates of Pb(II), Cr(III), Cd(II) and Se(IV) adsorption on the tailings were fast at the tested pH 6.5 and 9.0. Most of the metal adsorption was completed in 5 min. The high adsorption rates were likely attributed to the strong affinity of these metal ions to the iron oxide tailings surface.
- (6) Due to their low cost, relatively high adsorption rate and high removal capability, the waste iron oxide tailings has the potential to be utilized as adsorbents for cost-effective removal of heavy metals from water and wastewater.

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