

Adsorption of divalent manganese ion on manganese-coated sand

Po-Yu Hu, Yung-Hsu Hsieh, Jen-Ching Chen and Chen-Yu Chang

ABSTRACT

Locally available manganese-coated sand, from packing and a by-product of the filtration process for water treatment plants in Taiwan, was found to be a low cost and promising adsorbent for the removal of Mn^{2+} from raw water. In this work, adsorption and desorption of Mn^{2+} in water have been studied by using batch techniques. The equilibrium adsorption level was determined to be a function of the solution pH, contact time and adsorbate concentration. The equilibrium adsorption capacity of Mn^{2+} was obtained by using a pseudo-Langmuir isotherm. Ion exchange is probably one of the major adsorption mechanisms for binding divalent manganese ions to the coated sand. The results provide a feasible hypothesis of adsorption mechanisms. This study also supplies significant plant operation capacity data for engineering design.

Key words | adsorption capacity, filtration process, ion exchange, manganese-coated sand, pseudo-Langmuir isotherm

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INTRODUCTION

Over 30% of Taiwan's tap water comes from underground, making groundwater a vital resource owing to its wide dispersion and availability. Divalent ion constitutes the chief form of manganese in groundwater by virtue of complete attachment to soil and rocks, generating reductive and lightly acidic conditions. As an essential nutrient, manganese has few human diseases traced to it. Ordinary water contains different metals, depending on the geographic peculiarities of the watershed in any certain area, yet excessive manganese content can adversely affect daily life and/or industry, for example through bad taste, smell or colour of drinking water. Attaining a suitable concentration by reducing the manganese content in raw water presents a significant challenge in water treatment.

Traditionally, surplus dissoluble manganese ions in groundwater are removed by oxidation followed by rapid sand filtration. Insoluble tetravalent MnO_2 , formed via aeration, presents a reddish brown colour and a coating on silica sand previously packed in rapid sand filter. Coated material shows greater filter efficiency for soluble metal

ions in plain water than silica sand, known as 'manganese-coated sand' by filter operators. Such sand is a type of silica medium adsorbing manganese oxide on its surface during long-term filtration. Dissoluble ferrite and manganese ions manifest special properties of oxidation and adsorption, which have proved to be commercially beneficial as well. This higher oxidative state of manganese, a transition element, occurs on other manganese-rich surfaces in a specific system during autocatalysis; that is, the manganese oxide coating on quartz converted by manganese ions in an aquatic environment triggers a reaction of adsorptive oxidation (Morgan & Kessick 1975; Peter *et al.* 1997).

To date very limited research into adsorptive oxidation on dissoluble species, mechanisms, conditions of water and quality of environment have been published. This study develops a mechanism for interpreting the adsorptive oxidation of manganese-coated sand. We provide an understanding of its adsorptive properties, along with effects of various aquatic states on adsorption of manganese ions.

MATERIALS AND METHODS

Materials

Manganese-coated sand was collected from commercial product W-32 (serial number), and preparation was carried out under moderate temperature and acidic conditions by impregnation processes. Sand consists of grains with an average radius of 0.6–0.7 mm, specific gravity 2.4–2.5 and density 1.0 g ml^{-1} covered with a uniform, but friable, reddish brown coating. All solutions were prepared with deionized water (Milli-Q) and reagent-grade chemicals, stock cation solutions with Mn^{2+} standard solution. Those background electrolyte $NaNO_3$ concentrations were adjusted to 0.01, 0.05 and 0.1 M. Impure substances that could easily affect adsorption results were removed by the purification procedures.

Analyses

Physical characteristics of manganese-coated sand included BET specific surface area, micropore volume and pore size distributions. Other characteristics were determined by the nitrogen adsorption isotherm technique, with an ASAP 2010 micropore analyser (Micromeritics, USA). Zeta potential (ζ) measurements were performed with a zeta meter microelectrophoresis (Zeta-meter, Inc., Model 3.0, USA). Suspensions were prepared using 0.1 gram of manganese oxide peeled from manganese-coated sand in 1 l of deionized solution, pH adjusted using 0.1 M HNO_3 or $NaOH$ solutions while the solution was stirred. Then the solution was shaken for 24 hours. Four ζ measurements were performed for each sample, replacing the suspension after each measurement, with pH and temperature recorded.

Experiments

Adsorption kinetics experiments equilibrated accurately weighed 2.5 grams of manganese-coated sand in 50 ml of manganese ion solutions of known concentration. The initial concentration of manganese ions was held to 20 mg l^{-1} , and a pH of 5 ± 0.1 maintained throughout the

Table 1 | Specific surface areas/average pore diameter for manganese-coated sand

Phase	Surface area ($\text{m}^2 \text{ g}^{-1}$)	Average pore diameter (Å)
Unadsorbed	1.990	16.850
Adsorbed	2.191	16.026

experiments using dilute HNO_3 and $NaOH$ solutions. The solution was constantly stirred with a water bath shaker and the temperature kept at $25 \pm 1^\circ\text{C}$. Samples were taken at various times during a 24-h period. The residual concentration of manganese was determined by flameless atomic absorption spectrophotometry (Perkin-Elmer Analyst 100, USA).

For pH adsorption edges, the suspension pH was maintained within the range of 1.5–6. Adsorption isotherms were studied using $20\text{--}400 \text{ mg l}^{-1}$ of Mn^{2+} solution at a pH value of 3 ± 0.05 . The desorption experiments were conducted serially on previously equilibrated samples under adsorbing conditions over 4-, 16- and 24-hour spans, rapidly changing solution pH to 2.0 ± 0.1 ; reaction time lasted 1,440 min. Ferrite and manganese ions were mixed in the system, then competition experiments were conducted under the following concentrations of ferrite: 0, 10, 20 and 40 mg l^{-1} . Competition experiments were also performed under pH 5 ± 0.1 , samples taken as before. The effects of adsorption on ionic strength have also been probed at 0.01–0.10 M of $NaNO_3$.

RESULTS AND DISCUSSION

Specific surface area and pore size distribution analyses

Surface area and pore size distribution for samples were investigated using BET analysis. Specific surface areas for manganese-coated sand under unadsorbed and adsorbed Mn^{2+} ions are listed in Table 1. Pore size distribution of manganese-coated sand changed after reacting with Mn^{2+} ions and following oxidation; thus, some pores

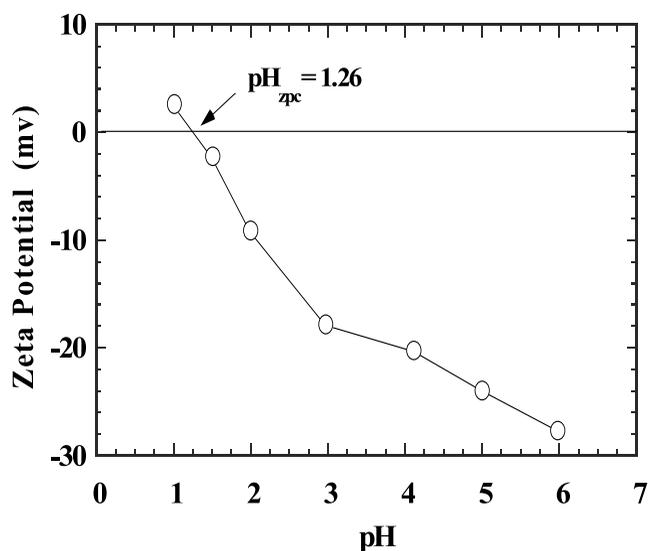


Figure 1 | Zeta potential of manganese oxide on coated sand for different pH ($I=0.01$ M; $T=25\pm 1^\circ\text{C}$).

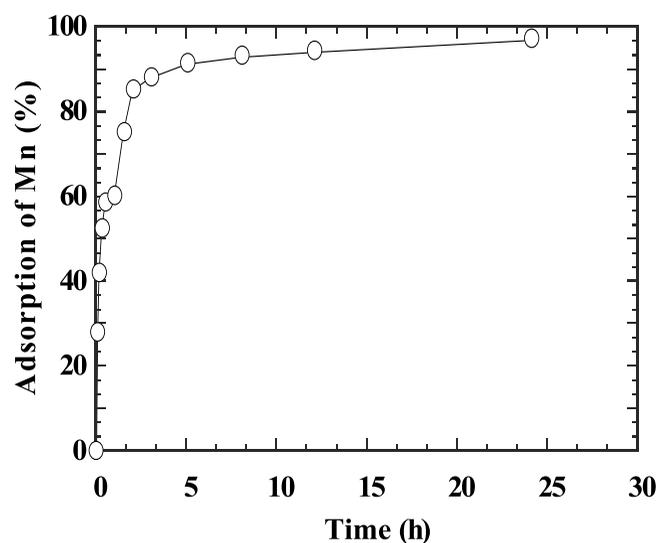


Figure 2 | Adsorption kinetics of Mn^{2+} on manganese-coated sand ($I=0.05$ M; $pH=5.23$; $T=25\pm 1^\circ\text{C}$).

changed through adsorption. Yet results indicate not only that micropores and parts of mesopores were saturated with Mn^{2+} ions but also that more active sites were formed by MnO_2 via oxidation. By contrast, the surface area of adsorbed manganese-coated sand increased from 1.990 to 2.191 m^2 per g sand after reacting with Mn^{2+} ions. Also, the pore size distribution of desorbed coated sand was similar to that of unadsorbed sand. Micropores and mesopores appeared again, while the surface area decreased from 16.850 to 16.026 m^2 per g sand.

The results indicate the possibility of slow oxidation of Mn^{2+} ions that could be adsorbed from surface sites of micro- and mesopores by regeneration of active sites with acid solution. Pore size distribution analyses therefore provided direct evidence for the results observed in Table 1, and supporting evidence for a slower oxidation rate of Mn^{2+} ions from manganese-coated sand. This suggests that the mechanisms of reaction involved pore diffusion and chemical reactivity.

Zeta potential measurement

Figure 1 shows the zeta potential of MnO_2 on coated sand for different pH values. Since variable charge results from

the protonation of manganese oxide, it should have a zero charge point where the positive charge is equal to the negative charge; the pH value of the point where net surface charge equals zero is called pH_{zpc} . The pH_{zpc} of MnO_2 is about 1.26, which conforms to similar results (1.5–4.6) from many past studies (Hearly *et al.* 1966). With most environmental pH values higher than the pH_{zpc} , the charge of coated sand is negative.

Adsorption kinetic tests

To further understand adsorption properties of manganese-coated sand for Mn^{2+} , this sand, which had the best adsorption efficiency, was used for adsorption kinetic experiments and adsorption isotherm studies. The purpose of kinetic tests was to measure the time needed for adsorption to reach equilibrium. Figure 2 displays the kinetic test results of Mn^{2+} at fixed pH and temperature. After adding Mn^{2+} to manganese-coated sand suspensions, residual concentration in the aqueous phase dropped immediately and decreased gradually with time. Pseudo-equilibrium of Mn^{2+} adsorption was attained within 4 hours, proving that manganese-coated sand adsorbed 96.7% up to final sampling time. Equilibrium

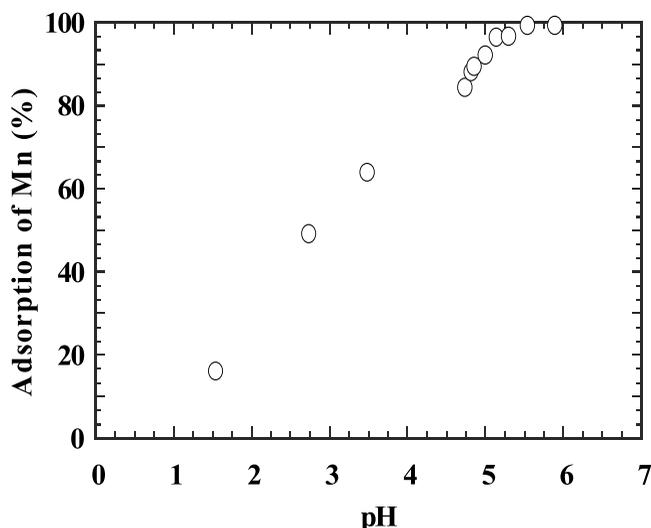


Figure 3 | Adsorption kinetics of Mn^{2+} on manganese-coated sand ($Mn^{2+}=20 \text{ mg l}^{-1}$; $I=0.05 \text{ M}$; $T=25 \pm 1^\circ\text{C}$).

was reached within 4 hours; 100% adsorption was not achieved. The residual concentration of Mn^{2+} did not significantly change between 4 and 24 h, so a 4-hour reaction time was chosen for isotherm experiments to ensure completion of the adsorption process.

Adsorption at different pH

Adsorption studies presented so far were carried out at pH 1.5–6. It is apparent from Figure 3 that Mn^{2+} adsorption is positively correlated with pH, approaching 100% at pH 5.53. The high dependency on pH for Mn^{2+} adsorption can be explained by the fact that pH affects the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate (Scott & Morgan 1996). Since pH_{zpc} of manganese oxide is about 1.26, experimental results could be interpreted with a negative charge for this mineral.

Adsorption isotherm

Figure 4 shows adsorption of Mn^{2+} with varying concentrations of adsorbent. With curves in the figure showing ‘S’ type adsorption, multilayer adsorption of Mn^{2+} can be

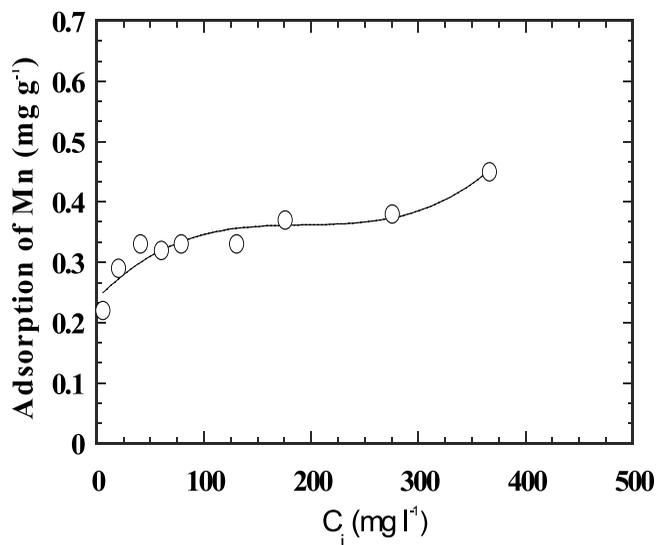


Figure 4 | Adsorption of Mn^{2+} at various equilibrium concentrations on manganese-coated sand ($pH=3 \pm 0.05$; $T=25 \pm 1^\circ\text{C}$).

predicted. Because adsorption has been carried out on manganese-coated sand, the following redox conversion yields oxide, providing new adsorption sites after Mn^{2+} has been oxidized. The results of adsorption density experiments are displayed in Figure 4. The equilibrium adsorption constant and maximum adsorption capacity for a pH value of 3 ± 0.05 were computed using a multilayer equation (Wang *et al.* 1998):

$$q = \frac{Q_m K_1 C}{(1 - K_2 C) [1 + (K_1 - K_2) C]} \quad (1)$$

where q (mg per g sand) is adsorbed density of Mn^{2+} per gram of coated sand, Q_m (mg per g sand) is the single layer adsorbed density and C (mg l^{-1}) is the residual concentration of Mn^{2+} after adsorption. K_1 is the equilibrium adsorption constant of the first layer; K_2 of the second layer. When K_2 equals zero, we have Langmuir's equation:

$$q = \frac{Q_m K_1 C}{1 + K_1 C} \quad (2)$$

A comparison of data between simulation and experiment is illustrated below. The multilayer equation

(pseudo-Langmuir isotherm) is shown as the equilibrium adsorption constant; K_1 and K_2 are 0.3543 and 0.0009412 l mg^{-1} , respectively, and the single layer adsorbed density (Q_m) value is 0.3805 mg per g sand.

$$q = \frac{1.348 \times 10^{-1} C}{(1 - 0.0009412 C)(1 + 0.3534 C)} \quad (3)$$

Adsorption values at the plateau in Figure 4 may serve as a gauge of the apparent maximum capacity of coated sand for testing Mn^{2+} adsorption, particularly because the low solubility of our test oxide precludes our discerning the maximum adsorption capacity of manganese-coated sand from adsorption isotherms.

Competition adsorption

Being abundant in dissoluble ferrite and manganese ions, groundwater benefits the application of manganese-rich surfaces to recognize competition adsorption of Fe^{2+} and Mn^{2+} in a coexisting system. To realize competition adsorption of Fe^{2+} and Mn^{2+} entirely, the system's pH condition should be observed clearly while avoiding the precipitation of iron oxide, which interferes with competition. According to the results in the previous tests, pH 3 is the lowest pH value at which the suspension is maintained in Fe^{2+} solution, and pH is determined for experimental conditions of competition adsorption.

Figure 5 illustrates the effects of Fe^{2+} on Mn^{2+} on manganese-coated sand. Final adsorption rate is about 62% (pH=3) in the system without Fe^{2+} . Solutions of 10 and 20 mg/l Fe^{2+} concentration to that of Mn^{2+} inhibited Mn^{2+} adsorption on manganese-coated sand by 56% and 52%, respectively, while such concentrations of Fe^{2+} inhibited adsorption by 13%, decreasing by 23%. In contrast, twice the Fe^{2+} concentration connected the system. Because Fe^{2+} exists in a solution whose chemical properties are quite similar to those of Mn^{2+} , its adsorption on to manganese-coated sand was affected by non-specific adsorption between MnO_2 and Mn^{2+} . With the presence of 10 mg l^{-1} Fe^{2+} , 83.8% maximum indicated manganese-coated sand reduced the adsorption density of both Mn^{2+} and Fe^{2+} .

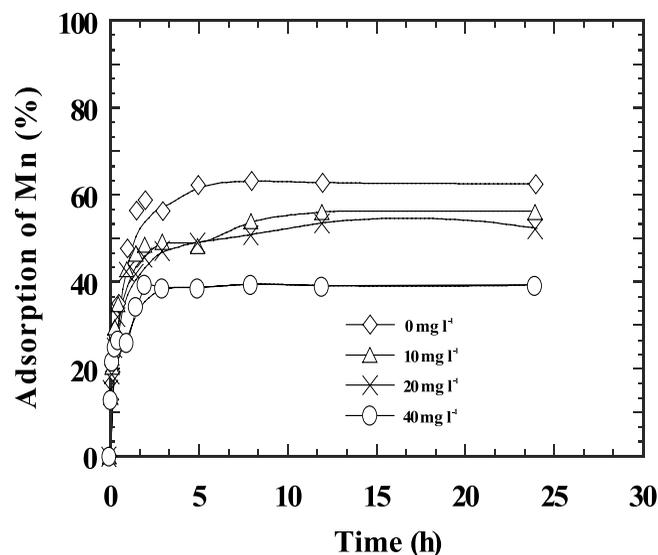


Figure 5 | Adsorption of Mn^{2+} on manganese-coated sand at various Fe^{2+} concentrations (pH=3±0.05; T=25±1°C).

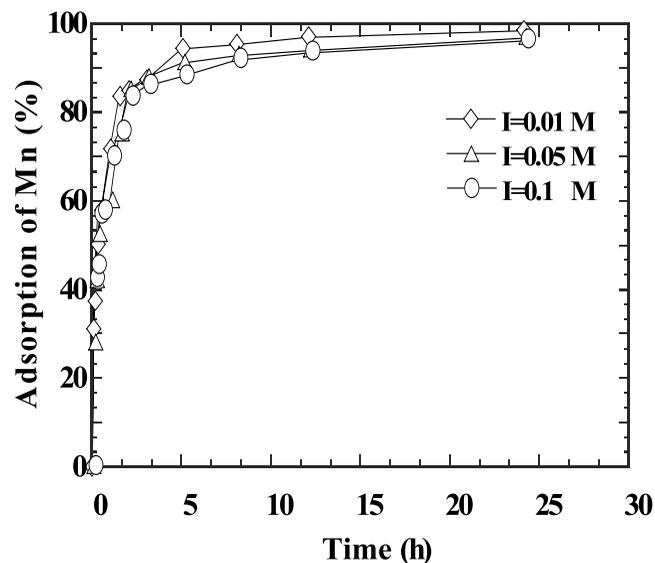


Figure 6 | Adsorption of Mn^{2+} on manganese-coated sand at various ionic strengths (pH=5±0.05; T=25±1°C).

Effects of ionic strength

Figure 6 depicts adsorption kinetics for 0.01 M, 0.05 M and 0.1 M ionic backgrounds. Ionic strength effect is negligible for these conditions, suggesting relatively strong interaction between ion and surface, characteristic of

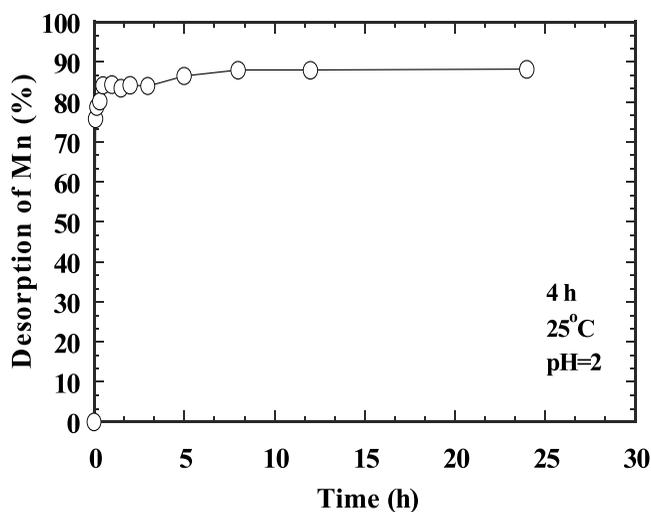


Figure 7 | Desorption of Mn^{2+} on manganese-coated sand at $pH=2\pm 0.05$ ($T=25\pm 1^\circ C$).

inner sphere complexes. In this case, however, single-layer simulation considering only inner layer reaction with free Mn^{2+} did not provide a suitable description of the data for each case.

Desorption experiments

Observed data for desorption at $pH\ 2.0 \pm 0.1$ are shown in Figure 7. Desorption is rapid in the first several minutes, then slows until it approaches 88%, attaining equilibrium in 30 min at an agitation speed of 100 rpm. Desorption capacity was slightly affected by the contact time of adsorption in 0.5–24 h intervals. The percentage of desorption was lower than 8% at 1,440 min. Compared with previous studies of acid/alkali resistance, these results hint that manganese-coated sand can be regenerated by acid solution. Knowledge of desorption behaviour provides a critical basis for understanding contaminant fate and transport. It is sensible to infer that the phenomenon of partial dissolvable oxide formed was conducted by oxidation on the surface of sand.

Kinetic data of desorption for various contact times are illustrated in Figure 8. For all test Mn^{2+} -manganese-coated sand combinations investigated, in more than 84% desorption increased sharply during the initial 30 min and reached an apparent plateau within 24 h. Representative

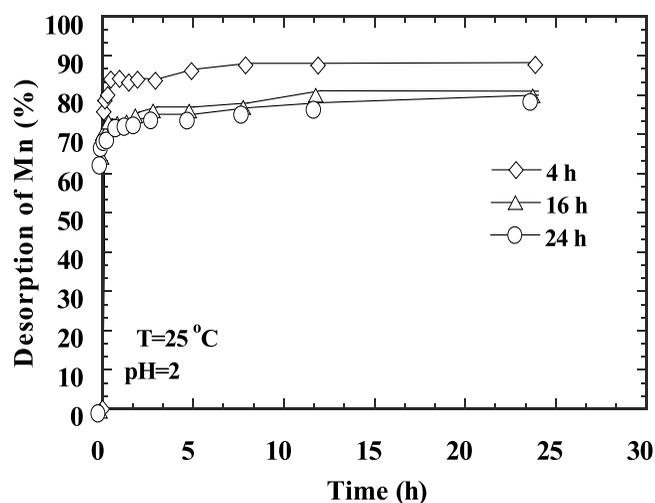


Figure 8 | Desorption rates for Mn^{2+} on manganese-coated sand ($pH=2\pm 0.05$; $T=25\pm 1^\circ C$).

graphs depict how desorbed mass diminished over time. According to research reported, slower desorption of ions from metal oxides suggests that the mechanism of reaction perhaps involves surface chemical reactivity. Thus, it can be inferred that slower desorption of Mn^{2+} ions on manganese-coated sand may be attributed to one or more additional mechanisms, for example, surface chemical reactivity. The results are in agreement with Jain and Ram (1997), who reported that lead and zinc ions were adsorbed by bed sediments of the river. This is attributed to a very slow diffusion of adsorbed metals from the surface film into micropores of newly formed oxide, the least accessible sites of adsorption.

Adsorption mechanism

Ion exchange may be the principal mechanism for the adsorption of Mn^{2+} . The adsorption sites affect the characteristics of metal oxides, and the major factor is determined by hydration (Hayes & Leckie 1987). From the nature of the metal oxides, which are efficient in capturing heavy metal ions, it can be speculated that protonation and deprotonation are the driving forces and that active sites are the charged surface of oxides. From the data from ζ measurements, electrostatic properties of metal oxides

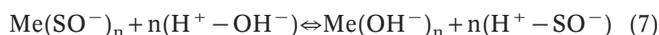
Table 2 | pH variation of Mn²⁺ adsorption on manganese-coated sand for 1,440 min (Mn²⁺ = 20 mg l⁻¹; initial pH = 5.23; T = 25 ± 1°C)

Sampling time	0	5	10	20	30	60	90	120	180	300	480	720	1,440
pH	5.23	4.49	4.58	4.67	4.90	5.11	5.56	6.73	7.02	7.17	7.19	7.20	7.24

under acidic conditions, ionization of water and active sites of oxides can be simulated by Equations (4) and (5):



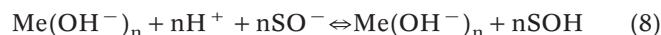
where S is the metal atom in the oxide, and SOH, SO⁻ and H⁺ are neutral, negatively charged oxide surface and proton, respectively. Based on the structure of manganese (hydr-)oxides, a possible mechanism of ion exchange could be considered as follows: a divalent manganese ion (Me) attaches itself to two adjacent hydroxyl groups and two oxyl groups which donate two pairs of electrons to Mn²⁺, forming saturated coordination number compounds and releasing two hydrogen ions into solution. Equations (6) and (7) illustrate the ion exchange between Mn²⁺ and active sites:



The equilibrium was quite dependent on pH. In most cases, adsorption of metal ions from solution ceased as the pH of the solution in contact with the adsorbent dropped to 3.0–3.5. When the pH was further lowered by any cause, for instance the introduction of acidic conditions, the equilibrium might be reversed. That is, ions were stripped from the solid into the solution. As a verification of the hypothesis that Mn²⁺ attaches itself to *n* hydroxyl active sites, releasing *n* hydrogen ions into solution, the theoretical pH change of supernatant was calculated from the experimentally verified change in Mn²⁺ concentration as adsorption occurred. Table 2 shows that if 20 mg of Mn²⁺ disappeared from 1 l of solution, hypothetically, it would produce 45.8 mg HNO₃ per litre for *n* = 2, with a

pH of about 3.14 by mass balance in Equation (7). However, the actual pH of the final solution in the experiment was 7.24, which is not in good agreement with the calculated value.

Equation 7 might be modified by experimental data. The residual concentration of Mn²⁺ in the aqueous phase dropped immediately and decreased gradually with time. Similar results of two-step adsorption, a rapid step followed by a much slower second step, have been reported for several metal/oxides systems (Yu *et al.* 2000). At the beginning of the kinetic test, pH decreased quickly and slowed down after 5 minutes. The observed decrease in pH was due to the hydrolytic reaction or ligand exchange between the functional group on the manganese oxide surface and Mn²⁺ in solution to release H⁺. This step is so fast that it could not affect the final regeneration of manganese (hydr-)oxides and Me(OH⁻)_{*n*} could be oxidized and converted to a new SOH of oxides:



Combined with Equations (6), (7) and (8), the ion exchange hypothesis as Equation (9) explains the better removal of Mn²⁺ from manganese-coated sand than from conventional silica:



In this case, acid is formed with the liberation of hydrogen ions, but HNO₃ is almost completely dissociated, while pH increased gradually to neutral.

CONCLUSIONS AND SUGGESTIONS

The following conclusions can be drawn based on investigation of Mn²⁺ removal by manganese-coated sand adsorption. First of all, the sand appears to be a promising

adsorbent for removal of Mn^{2+} from raw water. At these adsorption levels, a process using manganese-coated sand for the removal and recovery of Mn^{2+} is potentially more economical than current process technology. Second, adsorption of Mn^{2+} is dependent on its initial concentrations, time of contact and pH of the Mn^{2+} solution. Maximum removal of Mn^{2+} on coated sand occurs at a pH of about 5.0. Since different metals have different properties with regard to acidity of the solution, optimized pH for different metals removal may be very different. A further study on some other metals will be needed. Third, isothermal data on Mn^{2+} sorption on manganese-coated sand can be modelled by a pseudo-Langmuir isotherm. The capacity of sand for adsorption of Mn^{2+} can be calculated using these models. The adsorption capacity of Mn^{2+} for manganese-coated sand was 0.3805 mg per g sand. For other metals it may be very different.

ACKNOWLEDGEMENTS

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REFERENCES

- Hayes, K. F. & Leckie, J. O. 1987 Modeling ionic strength effect on anion adsorption at hydrous/solution Interfaces. *J. Colloid Interface Sci.* **115**, 564–572.
- Hearly, T. W., Herring, A. P. & Fuerstenau, D. W. 1966 The effect of crystal structure on the surface properties of a series of manganese dioxides. *Colloid Interface Sci.* **23**, 435–444.
- Jain, C. K. & Ram, D. 1997 Adsorption of lead and zinc on bed sediments of the river Kali. *Wat. Res.* **31**, 154–162.
- Morgan, J. J. & Kessick, M. A. 1975 Mechanism of autoxidation of manganese in aqueous solution. *Environ. Sci. Technol.* **9**, 157–159.
- Peter, J. L., Kenneth, S. J., Kenneth, H. C. & Virginia, A. E. 1997 Oxidation kinetics of manganese(II) in seawater at nanomolar concentrations. *Geochim. Cosmochim. Acta* **61**, 4945–4954.
- Scott, M. J. & Morgan, J. J. 1996 Reactions at oxides surface. 2. Oxidation of Se(IV) by synthetic birnessite. *Environ. Sci. Technol.* **30**, 1990–1996.
- Wang, J., Huang, C. P., Allen, H. E., Takiyama, L. R., Poespongoro, H. & Pirestani, D. 1998 Acid characteristics of dissolved organic matter in wastewater. *Wat. Environ. Res.* **35**, 1042–1048.
- Yu, B., Zhang, Y., Shuklab, A., Shuklac, S. S. & Dorris, K. L. 2000 The removal of heavy metal from aqueous solutions by sawdust adsorption-removal of copper. *J. Hazardous Mater.* **80**, 33–42.

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