

Adsorption of Zn^{2+} from solutions on manganese oxide obtained via ozone precipitation reaction

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Synthesis via ozone precipitation reaction was used to obtain manganese dioxide (OMD) and it was probed as an adsorbent for zinc ions. Adsorption was followed along shaking time and increasing ratio $[NO_3^-] / [Zn^{2+}]$, and isotherms were obtained at different pH values and in the presence of several anions (chloride, nitrate, sulphate, and acetate). It was found that adsorption equilibrium is fast and follows the pseudo-second order model ($q_e = 34 \pm 1$ mg/g and $K = 0.07 \pm 0.01$ g/mg h). Isotherms were fitted to Langmuir, Freundlich, and Langmuir-Freundlich models, and the best fitting was found with the last one. The process is dependent on pH and the efficiency increases from pH 1 to 4. The ratio $[NO_3^-] / [Zn^{2+}]$ up to 3 does not seem to change the behaviour of the process. Regarding the anions, the efficiency of Zn(II) adsorption occurs according to: acetate > nitrate and sulphate > chloride. Manganese oxide obtained via ozonization is an excellent adsorbent for zinc ions.

Keywords: manganese dioxide, aqueous Zn(II) solutions, adsorption process.

INTRODUCTION

Mainly, heavy metal pollutants present in the environment come through various sources including metal smelters, effluents from plastics, paper industries, microelectronics, mining operations, and the usage of fertilizers and pesticides, which can cause severe damage to human and aquatic life. Through adsorption, heavy metals only accumulate in top-soils in the case of relative low concentration; however, they will migrate to deep soil layers and further contaminate groundwater by rain water leaching or irrigation when the pollution level exceeds to a certain extent¹⁻².

A particular focus is given to innovative physical-chemical removal processes such as adsorption on new adsorbents, membrane filtration, electrodialysis, and photocatalysis³. The influence of several parameters as pH, initial concentration of metal ions, equilibrium contact time, and temperature, in order to get sorption equilibrium data has been tested by Langmuir and Freundlich models⁴⁻⁵.

Several studies about metal adsorption⁶⁻⁷ and equilibrium, dynamics and thermodynamic studies on adsorption of dyes⁸ provide use and application of sorption models and calculation of kinetic data.

Zinc is one of the most significant heavy metals often found in different effluents, it travels through the food chain via bioaccumulation, and is considered an essential element for life, but it can be toxic beyond permissible limits. The World Health Organization recommends that drinking water containing zinc at levels above 3 mg/L may not be acceptable to consumers⁹.

To date, zinc removal techniques include chemical precipitation, electrochemical treatment, ion exchange, membrane separation, adsorption, etc. Generally, adsorption has been and still is the most often used and studied method because it is cheap, effective, easily adopted, and a lot of such materials are well known for the efficient removal of Zn(II) from aqueous solutions¹⁰⁻¹².

In the search of novel, low-cost, and eco-friendly materials to remove Zn(II), there can be found numerous alternatives. In this sense, there is a continuous work related to adsorption of zinc onto manganese oxide compounds¹³⁻¹⁷. Then, it is noticed that the adsorption of zinc onto manganese oxide compounds is a complex process, often involving much more than simple ion exchange on the mineral surface. Factors such as the pH, the nature and concentration of the substrate and adsorbing ion, ionic strength, and the presence of competing and complexing ions all affect the amount of metal ions that will adsorb.

Manganese oxides are of considerable interest because of their high applicability in various fields like magnetic materials, energy transfer, redox catalysis, and battery materials. Due to their outstanding structural flexibility, novel chemical/physical properties, and abundance in nature, manganese oxides have been synthesized for a wide use as a catalyst, cathodic, and magnetic material¹⁸⁻²¹.

The synthesis of manganese oxide with a high purity is difficult because of precursor residues, and moreover, it is important to consider that all experimental parameters have significant influence on the resultant properties of the product. Ozone oxidation-precipitation has been presented as an excellent method for obtaining high purity manganese dioxide (OMD)²², and following this method, the retention property of OMD was probed for cadmium aqueous solutions²³. The aim of the present study was to explore the adsorption capacity of the metal ion Zn(II) on OMD. Batch experiments considered the following parameters: contact time between solid and aqueous phase, zinc cation concentration, the presence of different co-anions, and pH.

MATERIALS AND METHODS

The sorbent and solutions

In order to prepare OMD, ozone was flowed (Partial pressure $O_2-O_3 = 0.02$ atm, ozone flow: 1825 mg/h during 8 h and 25°C) through solutions of manganese sulphate ($[Mn^{2+}] = 5$ g/L) and 1M sulphuric acid; the yield of this process was >90%. A gamma type MnO_2 was obtained; details on the characterization of this compound are given elsewhere by Contreras²³.

Solutions of $ZnCl_2$, $ZnSO_4 \cdot 7H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Zn(CH_3COO)_2 \cdot 2H_2O$ were prepared with deionized water and stored in polyethylene bottles.

Zinc ion measurements

Zinc was analyzed by titration with ethylenediaminetetraacetic acid (EDTA) solutions and Erichrome Black T as indicator. At low concentrations, zinc was analysed using atomic absorption spectrometry (Varian, model Spectr AA20).

Sorption capacities for zinc ions at a specific shaking time (q_t) or at equilibrium (q_e) were calculated as the following:

$$q_t \text{ or } q_e = \frac{m(Zn^{2+})_I - m(Zn^{2+})_F}{m_{OMD}} = \frac{m(Zn^{2+})_{OMD}}{m_{OMD}} \quad (1)$$

where $m(Zn^{2+})_I$ and $m(Zn^{2+})_F$ are the initial and the final mass (in mg) of zinc ions in solution, respectively, and $m(Zn^{2+})_{OMD}$ and m_{OMD} are the mass (mg) of zinc ions sorbed by OMD and the mass (g) of OMD, respectively. The percentage of zinc ions in the sorbent was calculated as follows:

$$\%Zn_{adsorbed}^{2+} = \frac{m(Zn^{2+})_{OMD}}{m(Zn^{2+})_{initial}} \times 100 \quad (2)$$

Sorption studies

Batch system experiments were performed using 1g of OMD and 100 mL several zinc salt solutions. Flasks were shaken in a 30°C water bath, with 240 rpm orbital shaking. The pH was continuously monitored and adjusted when necessary with solutions of KOH (0.5 M) and/or the acid corresponding to the experimental anion (chloride, nitric, sulfuric, or acetic). Later, the samples were filtered through Millipore membranes. The zinc ions in the solution were determined after contact as described in the previous section.

For kinetic studies mixtures of OMD and 0.0275 M $ZnSO_4$ (1800 mg/L of Zn^{2+}), solutions were vigorously shaken for different lengths of time, from 10 minutes to 3 h. The pH value for these experiments was 4.7 ± 0.1 . All other experiments were carried out by shaking for 2 h.

The study of the effect of nitrate ions on the system was performed with 0.0275 M $Zn(NO_3)_2 \cdot 6H_2O$ (1800 mg/L of Zn^{2+}) solutions to which KNO_3 was added up to ratios $[NO_3^{1-}] / [Zn^{2+}]$, which were 2.6, 2.8 and 3. The pH value was 2.7 ± 0.1 .

The isotherm studies were carried out with initial concentrations from 25 mg/L to 2000 mg/L ($4 \times 10^{-4} - 3 \times 10^{-2}$ M) for $ZnCl_2$, $ZnSO_4 \cdot 7H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$, and from 25 to 2500 mg/L ($4 \times 10^{-4} - 4 \times 10^{-2}$ M) for $Zn(CH_3COO)_2 \cdot 2H_2O$. The pH value was 2.3 ± 0.1 .

The experiments on the effect of pH were carried out with OMD and $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solutions whose pH values were adjusted to 1, 2.3, and 4.

RESULTS

The adsorption occurs during the first few minutes because the macropore diffusion is quick and the boundary-layer effect can be considered as minimal for $t < 10$ minutes, and then the equilibrium condition is attained. The maximal percentage of adsorption was $91.2 \pm 0.4\%$. The pH of equilibrium for these experiments was 4.7 ± 0.1 .

Experimental q_t data as a function of time were well fitted to the pseudo-second order model (see Fig. 1). The software Statistica 6.0 was used for the nonlinear regression analysis. The nonlinear form of this model can be represented by the following equation:

$$q_t = \frac{Kq_e^2 t}{1 + Kq_e^2 t} = \frac{81t}{1 + 2.4t} \quad (r^2 = 0.99) \quad (3)$$

where q_t (mg/g) is the amount of zinc ions sorbed at time t (h), K (g/mg h) is the pseudo-second order constant and q_e (mg/g) is the amount of zinc ions sorbed at equilibrium. The values obtained were: $q_e = 34 \pm 1$ mg/g and $K = 0.07 \pm 0.01$ g/mg h.

The pseudo-second-order rate model is based on the assumption that the rate-limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate²⁴⁻²⁵. Then, sorption of Zn(II) on OMD may be considered as a chemisorption. This model considers as well that one adsorbate molecule is adsorbed onto two active sites²⁶. Adsorption of Zn^{2+} has followed as well this kinetic behavior for sorbents like calcinated loess²⁷ and an amorphous hydrous manganese oxide¹⁶.

The experiments done with an increasing concentration of nitrate ions ($[NO_3^-] : [Zn^{2+}] = 2.6, 2.8, \text{ and } 3$) showed that the sorption capacity was constant ($q_e = 19.6$ mg/g) in this interval.

The data obtained for the isotherms were fitted to the models of Langmuir, Freundlich, and Langmuir-Freundlich in order to describe the zinc ion sorption behavior by manganese oxide. The software Statistica 6.0 was used for the nonlinear regression analysis. Table 1

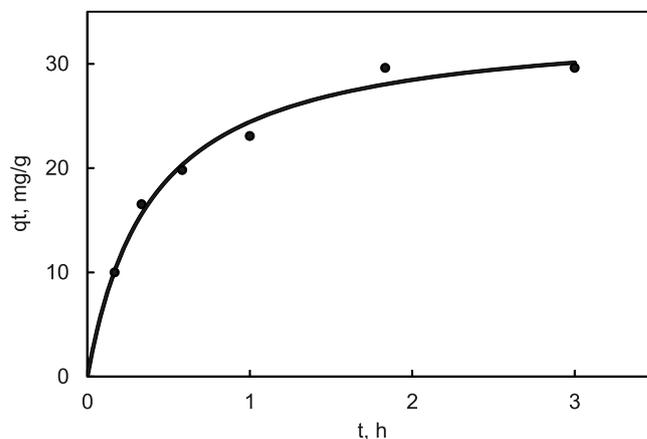


Figure 1. Zinc ion sorption from aqueous solutions by manganese dioxide as a function of time. The line correspond to the fitting to the pseudo-second order model

Table 1. Effect of different anions on the sorption system: Zn(II) – manganese oxide

Model	Parameter	Cl ⁻ [n = 13]	SO ₄ ²⁻ [n = 14]	NO ₃ ⁻ [n = 12]	COO ⁻ [n = 24]
Langmuir $q_e = \frac{q_0 b C_e}{1 + b C_e}$	*1 _{q_e}	10.6 ± 0.3	11.7 ± 0.4	11.6 ± 0.5	19.1 ± 0.7
	*2 _{K_L}	0.009 ± 0.001	0.012 ± 0.003	0.01 ± 0.002	0.004 ± 0.001
	R ²	0.97	0.93	0.95	0.96
Freundlich $q_e = K_F C_e^{1/n_F}$	*3 _{K_F}	1.5 ± 0.3	1.8 ± 0.4	1.1 ± 0.2	1.1 ± 0.2
	n _F	3.8 ± 0.4	3.9 ± 0.4	3.1 ± 0.2	2.7 ± 0.1
	R ²	0.93	0.93	0.96	0.96
Langmuir-Freundlich $q_e = \frac{K_{LF} C_e^{1/n_{LF}}}{1 + a C_e^{1/n_{LF}}}$	*3 _{K_{LF}}	0.3 ± 0.1	0.7 ± 0.4	0.5 ± 0.2	0.5 ± 0.2
	n _{LF}	1.3 ± 0.2	1.7 ± 0.4	1.7 ± 0.1	1.7 ± 0.1
	a	0.02 ± 0.01	0.05 ± 0.02	0.03 ± 0.01	0.02 ± 0.003
	1/n _{LF}	0.76	0.60	0.60	0.60
	R ²	0.98	0.95	0.97	0.97

*1: Total amount of zinc ions sorbed at equilibrium (mg g⁻¹).

*2: Langmuir constant (L mg⁻¹).

*3: Freundlich and Langmuir-Freundlich constants, respectively (L(1/n) g⁻¹ · mg(1/n)⁻¹).

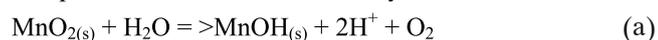
shows the results obtained. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter: $R_L = 1 / (1 + K_L C_0)$, where K_L is the Langmuir isotherm constant (given in Table 1) and C_0 is the initial concentration of zinc (mg/L). The values of R_L , calculated according to this equation for all the anions studied, were between 0.82(±0.06) and 0.06(±0.02) for C_0 from 25 to 2000 or 2500 mg/L, according to each anion. The R_L values that lie between 0 and 1 indicate favourable conditions for sorption.

The values of $1/n_F$ calculated by the Freundlich model, which lie in the range of 0.1 and 1.0 (Table 1), confirm the favourable conditions of sorption and imply heterogeneous surface structure with minimum interaction between the adsorbed atoms.

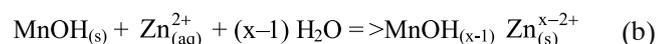
The highest R^2 values were found for the Langmuir-Freundlich model (Table 1); the values of $1/n_{LF}$ lie in the range of 0.1 and 1.0 as well. The differences of K_F and K_{LF} values are due to differences of the parameter $1/n$ for both models. Slight differences were appreciated for the presence of chloride, sulphate and nitrate anions; however acetate ions seem favour the zinc adsorption (see Fig. 2).

Isothermal, as well as kinetic behaviours suggest that the main mechanism involved in zinc sorption by OMD is chemisorption on heterogeneous material, but not necessarily on a multilayer.

The expressions that describe the formation of surface complexes on oxide surfaces may be:



and



which imply that the formation of the surface complex on OMD results in the release of protons, and the quantity of these protons depends on the real chemical species in solution.

According to diagrams of chemical species²⁸ and considering the conditions of the present research, the following is observed: Zn^{2+} is the unique species in nitrate media (pH between 2 and 6.5) and for acetate media at pH = 2.3. For pH = 2.3 and chloride media: Zn^{2+}

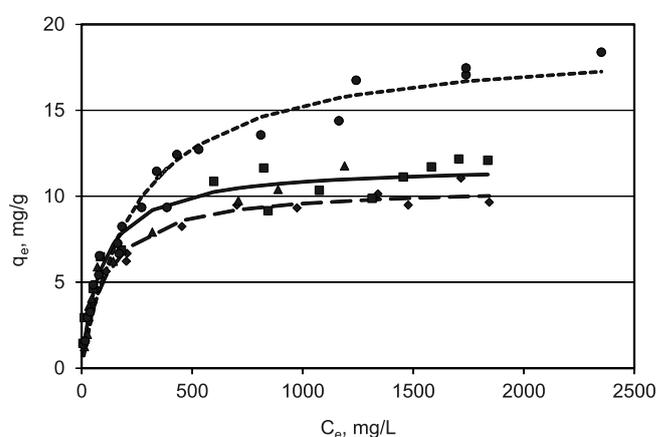


Figure 2. Zinc ion sorption from aqueous solution by manganese dioxide: effect of anions on the isotherms. Circles: acetate. Triangles: nitrate. Squares: sulphate. Rhombes: chloride. The lines correspond to the fittings to the Langmuir-Freundlich model

(95%) and ZnCl^+ (5%) are present; whereas for sulphate media and pH between 2.3 and 5, the present species are: Zn^{2+} (70%), ZnSO_4 (22%) and ZnSO_2^{2-} (8%). In this last media, it is quite possible that adsorption is partially due to the precipitation of the zinc sulphate.

The values of Langmuir q_e are intrinsic of the system sorbent-sorbate and typical of the experimental conditions. However, the q_e values obtained in the present work by the fitting with the Langmuir model (Tables 1 and 2) are similar to some values previously reported; for instance: a) $q_e = 16.3$ mg/g for a MnO_2 -modified diatomite¹⁷; b) $q_e = 0.98$ mmol/g (64 mg/g), at pH = 4 and nitrate media for a synthetic manganese oxide¹⁶ and; c) $q_e = 0.83$ mmol/g (55 mg/g), at pH = 4 and nitrate media for a hydrous manganese oxide²⁹.

The data on the effect of the pH (Table 2 and Fig. 3) for the adsorption of Zn from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solutions were fitted by the above-mentioned method, and the best fit was obtained by the Langmuir-Freundlich model as well. The increase of the adsorption efficiency (q_e) with pH is notorious for all three models applied. This effect had been observed previously in the literature for zinc adsorption onto amorphous hydrous manganese dioxide¹³. However, a comparison of the values of q_e of Table II with the above value for the experiments done

Table 2. Effect of pH on the sorption system: Zn(II) – manganese oxide

Model	Parameter	pH = 1	pH = 2.3	pH = 4
Langmuir $q_e = \frac{q_0 b C_e}{1 + b C_e}$	¹ q _e	7±1	11.6±0.6	41±2
	² K _L	0.002±0.001	0.012±0.002	0.016±0.005
	R ²	0.82	0.94	0.88
Freundlich $q_e = K_F C_e^{1/n_F}$	³ K _F	0.2±0.1	1.5±0.2	9.4±0.7
	n _F	2.3±0.4	3.5±0.2	5±0.3
	1/n _F	0.43±0.09	0.28±0.02	0.2±0.01
	R ²	0.84	0.97	0.99
Langmuir- Freundlich $q_e = \frac{K_F C_e^{1/n_{LF}}}{1 + a C_e^{1/n_{LF}}}$	³ K _{LF}	0.025±0.008	0.9±0.3	7±1
	n _{LF}	0.9±0.1	0.5±0.1	0.36±0.05
	1/n _{LF}	1.1±0.1	2±0.1	2.8±0.1
	a	0.003±0.001	0.048±0.008	0.1±0.01
	R ²	0.82	0.98	0.994

*1: Total amount of zinc ions sorbed at equilibrium (mg g⁻¹).

*2: Langmuir constant (L · mg⁻¹).

*3: Freundlich and Langmuir-Freundlich constants, respectively (L(1/n) g⁻¹ mg(1/n)⁻¹).

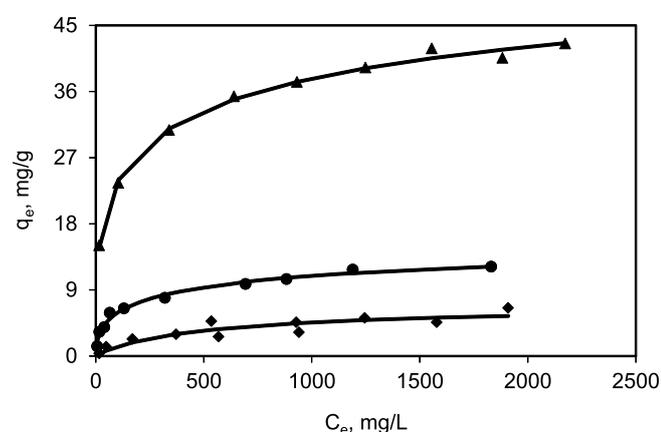


Figure 3. Zinc ion sorption from aqueous solution by manganese dioxide: effect of pH on the isotherms: Triangles: pH = 4. Circles: pH = 2.3. Rhombes: pH = 1. The lines correspond to the fittings to the Langmuir-Freundlich mode

with an increasing concentration of nitrate ions [NO₃⁻] : [Zn²⁺] and pH = 5 (q_e = 19.6 mg/g) do not change due to the excess of nitrate ions.

CONCLUSIONS

The adsorption of Zn(II) on OMD occurs during the first few minutes of contact because the macropore diffusion is quick and the boundary-layer effect can be considered as minimal. Adsorption of Zn²⁺ followed the kinetic behavior of the pseudo-second order, which describes that the rate-limiting step may be chemisorption that involves valence forces through sharing or exchange of electrons between OMD and Zn(II). The isotherms were well fitted to the Langmuir-Freundlich model. Isothermal as well as kinetic behaviors suggest that the main mechanism involved in zinc sorption by OMD is chemisorption on heterogeneous material but not necessarily on a multilayer. For nitrate and chloride media adsorption can be explained by means of the formation of surface complexes. Regarding the zinc anions, the efficiency occurs according to: acetate > nitrate and sulphate > chloride. Manganese oxide obtained via ozonization is an excellent adsorbent for zinc ions.

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LITERATURE CITED

- Fu, F. & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manag.* 92, 407–418. DOI: 10.1016/j.jenvman.2010.11.011.
- Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L. & Zhang, Q. (2012). Heavy metal removal from water/wastewater by nanosized metal oxides: A review. *J. Hazard. Mater.* 211–212, 317–331. DOI: 10.1016/j.jhazmat.2011.10.016.
- Barakat, M.A. (2011). New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem.* 4, 361–377. DOI: 10.1016/j.arabjc.2010.07.019.
- Khan, T.A., Singh, V. & Ali, I. (2009). Sorption of Cd(II), Pb(II), and Cr(VI) metal ions from wastewater using bottom fly ash as a low cost sorbent. *J. Environ. Prot. Sci.* 3, 124–132. <http://aes.asia.edu.tw/Issues/IEPS2009/KhanTA2009a.pdf>
- Ali, I., Asim, M. & Khan, T.A. (2012). Low cost adsorbents for the removal of organic pollutants from wastewater. *J. Environ. Manag.* 113, 170–183. DOI: 10.1016/j.jenvman.2012.08.028.
- Khan, T.A., Nazir, M., Ali, I. & Kumar, A. (2013). Removal of chromium(VI) from aqueous solution using guar gum–nano zinc oxide biocomposite adsorbent. *Arab. J. Chem. (In press)*. DOI: 10.1016/j.arabjc.2013.08.019.
- Khan, T.A., Chaudhry, S.A. & Ali, I. (2015). Equilibrium uptake, isotherm and kinetic studies of Cd(II) adsorption onto iron oxide activated red mud from aqueous solution, *J. Mol. Liq.* 202, 165–175. DOI: 10.1016/j.molliq.2014.12.021.
- Khan, T.A., Dahiya, S. & Ali, I. (2012). Use of kaolinite as adsorbent: Equilibrium, dynamics and thermodynamic studies on the adsorption of Rhodamine B from aqueous solution, *Appl. Clay Sci.* 69, 58–66. DOI: 10.1016/j.clay.2012.09.001.
- World Health Organization (WHO). (2011). *Guidelines for drinking water quality* (4th Ed.) 433–434. ISBN: 978 92 4 154815 1.
- Bhattacharya, A.K., Mandal, S.N. & Das, S.K. (2006). Adsorption of Zn(II) from aqueous solution by using different adsorbents. *Chem. Eng. J.* 123, 43–51. DOI: 10.1016/j.cej.2006.06.012.
- Carrott, P.J.M., Ribeiro-Carrot, M.M.L., Nabais, J.M.V. & Prates-Ramalho, J.P. (1997). Influence of surface ionization on the adsorption of aqueous zinc species by activated carbons. *Carbon.* 35, 403–410. DOI: 10.1016/S0008-6223(97)89611-X.

12. Silber, A., Bar-Yosef, B., Suryano, S. & Levkovitch, I. (2012). Zinc adsorption by perlite: Effects of pH, ionic strength, temperature, and pre-use as growth substrate. *Geoderma* 170, 159–167. DOI: 10.1016/j.geoderma.2011.11.028.
13. Kanungo, S.B., Tripathy, S.S., Mishra, S.K. & Sahoo, B. (2004). Adsorption of Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} onto amorphous hydrous manganese dioxide from simple (1-1) electrolyte solutions. *J. Colloid Interf. Sci.* 269(1), 11–21. DOI: 10.1016/j.jcis.2003.07.002.
14. Tonkin, J.W., Balistrieri, L.S. & Murray, J.W. (2004). Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. *Appl. Geochem.* 19, 29–53. DOI: 10.1016/S0883-2927(03)00115-X.
15. Pan, G., Qin, Y., Li, X., Hu, T., Wu, Z. & Xie, Y. (2004). EXAFS studies on adsorption-desorption reversibility at manganese oxides-water interfaces. I. Irreversible adsorption of zinc onto manganite ($\gamma\text{-MnOOH}$). *J. Colloid Interf. Sci.* 271, 28–34. DOI: 10.1016/j.jcis.2003.11.028.
16. Della-Puppa, L., Komárek, M., Bordas, F., Bollinger, J.C. & Joussein, E. (2013). Adsorption of copper, cadmium, lead and zinc onto a synthetic manganese oxide. *J. Colloid Interf. Sci.* 399, 99–106. DOI: 10.1016/j.jcis.2013.02.029.
17. Caliskan, N., Kul, A.R., Alkan, S., Sogut, E.G. & Alacabey, I. (2011). Adsorption of Zinc(II) on diatomite and manganese-oxide-modified diatomite: A kinetic and equilibrium study. *J. Hazard. Mater.* 193, 27–36. DOI: 10.1016/j.jhazmat.2011.06.058.
18. Chen, H., Chu, P.K., He, J., Hu, T. & Yang, M. (2011). Porous magnetic manganese oxide nanostructures: Synthesis and their application in water treatment. *J. Colloid Interf. Sci.* 359, 68–74. DOI: 10.1016/j.jcis.2011.03.089.
19. Bastami, T.R. & Entezari, M.H. (2012). Synthesis of manganese oxide nanocrystal by ultrasonic bath: Effect of external magnetic field. *Ultrason. Sonochem.* 19, 830–840. DOI: 10.1016/j.ultrasonch.2011.11.019.
20. Sun, M., Lan, B., Yu, L., Ye, F., Song, W., He, J., Diao, G. & Zheng, Y. (2012). Manganese oxides with different crystalline structures: Facile hydrothermal synthesis and catalytic activities. *Mater. Lett.* 86, 18–20. DOI: 10.1016/j.matlet.2012.07.011.
21. Lu, B., Chen, S. & Kawamoto, K. (2012). Direct hydrothermal synthesis of nanosized mesoporous ramsdellite manganese oxide with high surface area. *Mater. Res. Bull.* 47, 3619–3624. DOI: 10.1016/j.materresbull.2012.06.052.
22. Kijima, N., Yasuda, H., Sato, T. & Yoshimura, Y. (2001). Preparation and characterization of open tunnel oxide $\alpha\text{-MnO}_2$ precipitated by ozone oxidation. *J. Solid State Chem.* 159, 94–102. DOI: 10.1006/jssc.2001.9136.
23. Contreras R. & Lapidus G.T. (1999). Combined water and the ion exchange characteristics of manganese dioxide produced by ozonation. *J. Colloid Interf. Sci.* 213, 251–267. DOI: 10.1006/jcis.1999.6114.
24. Ho Y.S. & McKay G. (1999). Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451–465.
25. Ho Y.S. (2006). Review of second-order models for adsorption systems. *J. Hazard. Mater.* B136, 681–689. DOI: 10.1016/j.jhazmat.2005.12.043.
26. Khan T.A., Khan, E.A. & Shahjahan. (2015). Removal of basic dyes from aqueous solution by adsorption onto binary iron-manganese oxide coated kaolinite: Non-linear isotherm and kinetics modeling. *Appl. Clay Sci.* 107, 70–77. DOI: 10.1016/j.clay.2015.01.005.
27. Tang, X., Li, Z. & Chen, Y. (2009). Adsorption behaviour of Zn (II) on calcinated Chinese loess. *J. Hazard. Mater.* 161(2), 824–834. DOI: 10.1016/j.hazmat.2008.04.059.
28. Puigdomenech, I. (2010). *Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA)*, Royal Institute of Technology, Inorganic Chemistry. 10644 stockholm Sweden. ignasi@inorg.kth.se
29. Su, Q., Pan, B., Wan, S., Zhang, W. & Lv, L. (2010). Use of hydrous manganese dioxide as potential sorbent for selective removal of lead cadmium and zinc ions from water. *J. Colloid Interf. Sci.* 349(2), 607–612. DOI: 10.1016/j.jcis.2010.05.052.