Adsorption properties of Kemerovo manganese ore toward zinc

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Abstract. Zinc is a toxic and a prevailing pollutant contained in wastewater in nonferrous metallurgy. With a view to ensuring the environmental safety, it is required to develop an integrated wastewater treatment technology to remove heavy metals from effluents. A promising approach to natural and waste water treatment is adsorption using various natural materials. The author analyzes the adsorption capacity of manganese ore from Durnovskoe and Usa deposits toward zinc in static conditions. The adsorption isotherms are described by the Langmuir equation at a high correlation factor. The maximal adsorption capacity, the sorption equilibrium constant and the change in the Gibbs energy are evaluated. Usa manganese ore reveals higher adsorption capacity toward zinc.

1. Introduction
Zinc (Zn) is a common (percent abundance 0.008) commercially important but toxic metal (all Zn compounds belong to hazard class III). Zinc MAC in domestic and fishery water bodies is 1 and 0.001 mg/dm³, respectively [1, 2]. Long-term intake of zinc above the sanitary standard by a human organism promotes bone loss and malignant neoplasms. Zinc enters natural water as a result of natural fracture and dissolution of rocks and minerals (spalhellite, red zinc, zinc sulphate, zinc spar, cadmia), as well as with effluents of processing and electroplating plants, parchment paper production, ink making, viscose fiber manufacturing, etc. [3]. In oxidation zones in sulfide deposits, Zn concentration in acid water can reach 1–5 g/dm³. Many iron and rare earths mining and processing plants skip the spalhellite concentration production, and ZnS goes to tailings or sulphide middlings to be stored. On ground surface, Zn becomes more mobile. Spalhellite blooms out and contaminates water sources with Zn. For example, at magnetite deposits, Zn content in tailings grows more than 10 times; in complex sulphide ore deposits, Zn content in tailings reaches 0.3%. Tailings at such deposit accumulate up to 4 kt of Zn per annum. Zn content in effluents of various productions is (mg/dm³): lead-and-zinc processing plants—0.06–1.54 after sulphide ore flotation, 0.25–4.4 after oxidized ore flotation, 0.16–0.44 after tailings pond; lead-and-zinc mine water—0.2–5000; nonferrous metallurgy processing plants—40–50 [1, 2].

At many mining and processing plants, wastewater treatment efficiency is insufficient to ensure quality standard of discharge in surface water bodies due to worn-out equipment and obsolete technologies. In view of the environmental requirements, it is necessary to develop an integrated wastewater treatment technology to remove ions of heavy metals from wastewater. A promising approach to natural and waste water treatment is adsorption with various natural materials. Manganese and ferrous oxides are known to possess high adsorptive capacity toward many metals. Low-grade and rebellious
manganese ore (containing Mn and Fe oxides), common everywhere in the world, shows adsorption activity toward ions of heavy metals and arsenic compounds [4–7].

2. Adsorption capacity of manganese ore

Aimed to push application limits of mineral raw materials regarding improved waste water treatment, it was decided to analyze adsorption properties of manganese ore from Durnovskoe and Usa deposits in the Kemerovo Region toward zinc.

X-ray structural analysis of Durnovskoe ore shows predominance of kriptomelan $\text{KMn}_8\text{O}_{16}$ with the presence of hematite $\text{Fe}_2\text{O}_3$ and quartz $\text{SiO}_2$. It is possible that kriptomelan is associated with psilomelan (variable composition mineral $\text{mMnO} \cdot \text{MnO}_2 \cdot n\text{H}_2\text{O}$). Usa deposit is mainly composed of calcite $\text{CaCO}_3$ with the presence of rhodochrosite $\text{MnCO}_3$, ganophyllite (micaceous silicate Mn of hydromica type), some quartz and hausmannite $\text{MnMn}_2\text{O}_4$.

Preliminary treated ore exhibits higher adsorption activity [6]. Durnovskoe ore was subjected to preliminary magnetic separation, which increased concentration of Mn and Fe from 16.36 to 36.53% and from 11.46 to 17.13%, respectively (Figure 1a). Usa ore calcinations at $t = 600 \, ^\circ \text{C}$ provided no observable change in the composition of elements (Figure 1b) but resulted in essential structural changes. Namely, rhodochrosite disappeared (decomposition of carbonates took place) while the phases of hausmannite and ganophyllite, which are active oxide forms of Mn, increased. In this study, we used ore sample treated using the described methods. Adsorption capacity of manganese ore toward Zn was assessed in static conditions using the procedure from [8].

![Figure 1](image-url)

**Figure 1.** Composition of elements in original and treated manganese ore: (a) Durnovskoe ore; (b) Usa ore.

An important stage in the analysis of adsorption capacity of a sorbent is the adsorption isotherms. The isotherms were plotted by the method of variable concentrations. A model solution prepared using tap water added with zinc sulfate (Zn content 1–60 mg/dm$^3$) was poured in a flask, added with manganese ore sample 2 g/dm$^3$ in weight and treated on magnetic stirrers at the air temperature of 25 $^\circ\text{C}$ for 30 minutes. After that, the sorbent was filtered off, and residual zinc concentration $C_{\text{eq}}$ was determined in the filtrate. The obtained data were used to calculate the adsorption capacity $A$ of ore toward to toxicant. The maximal adsorption capacity $a_m$ of Durnovskoe and Usa ore toward zinc is 4.04 and 8.89 mg/g, respectively (Figures 2a and 2c).

According by Giles’s classification of adsorption isotherms [9], the obtained adsorption curves of zinc at Durnovskoe and Usa manganese ore belong to class L (Langmuir isotherms, concave curves relative to the concentration axis, surface is saturated with growing concentration—L2 isotherm) and to class H (high affinity adsorption, initially nearly vertical curve), respectively. The equilibrium of the solution–solid phase system where sorption processes run at constant temperature and in constant volume can be described with various equations of adsorption isotherm. The obtained adsorption isotherms can be represented by the Langmuir equation for isotherms in all ranges of equilibrium concentrations [3]:

$$K_L = \frac{a_m C_{\text{eq}}}{(1 + K_L C_{\text{eq}})^2}$$
where \( A_{\text{max}} \) is the maximum adsorption, Langmuir monolayer capacity, mg/l, \( K_L \) is the adsorption equilibrium constant characterizing the bonding strength between an element and the adsorption site.

For finding \( A_m \) and \( K_L \), the obtained relations were converted into a linear form as per:

\[
\frac{C_{\text{eql}}}{A} = \frac{C_{\text{eql}}}{A_{\text{max}}} + \frac{1}{K_L A_{\text{max}}},
\]

i.e., linear dependence of \( C_{\text{eql}}/A \) on \( C_{\text{eql}} \).

The linear isotherm illustrates suitability (or unsuitability) of a chosen equation to the experimental data and allows prompt assessment of the parameters by the plot slope and cutoff. Figures 2b and 2d show the zinc adsorption isotherms in the linear coordinates. The data are compiled in Table 1.

**Table 1.** Zinc adsorption at Durnovskoe and Usa manganese ore in the experiment and in calculations using the Langmuir equation and the Gibbs energy

| Manganese ore deposit | \( a_m, \) mg/g (experiment) | \( K_L \) | \( A_m, \) mg/g | \( R^2 \) | \( \Delta G \), kJ/mole |
|-----------------------|-------------------------------|----------|----------------|------|-------------------|
| Durnovskoe            | 4.04                          | 0.481    | 4.185          | 0.999| -25.66            |
| Usa                   | 8.89                          | 5.840    | 8.92           | 0.999| -31.84            |

*correlation factor
Apparently, the Langmuir equation describes well and at high correlation factor the equilibrium condition of zinc adsorption at manganese ore from both deposits. By the Langmuir theory, adsorption occurs at active centers (such centers in manganese ore can be Mn and Fe oxides, as well as the edges and angles of crystals and boundaries of grains at which especially intense force fields are generated; or crystal structure ruptures); interaction between adsorbed ions is absent; adsorption runs as a monolayer and reaches maximum at complete saturation of the monolayer [10].

The chemical affinity between the reacting substances was assessed from the Gibbs energy change $\Delta G$, J/mole [9]:

$$\Delta G = -RT \ln K_L,$$

where $R$ is the gas constant, $R = 8.314$ J/(mole·K); $T$ is the reaction temperature, K.

The resultant values of $\Delta G < 0$ (see Table 1) are reflective of the chemical interaction between zinc ions and ore. With more negative value of $\Delta G$, the system is farther from the equilibrium and is more reactive. In the case under discussion, the highest affinity toward zinc is exhibited by Usa ore.

A direct influence on adsorption is exerted by acid-base balance of the water phase. The dependence of adsorption efficiency of metal cations on water pH is illustrated, in particular, by the preferred adsorption of their hydrolyzed forms as against free ion of metal. Figure 3 show the distribution of zinc forms in water solution subject to its pH.

![Figure 3. Forms of Zn in solution (1.0 mg/dm³) as function of pH [3].](image)

In the range of pH from 5 to 7, zinc is totally in the ionic condition—Zn$^{2+}$. At pH higher than 7, hydrolyzed ion ZnOH$^+$ is formed and reaches its maximum of 10% of total quantity of zinc in solution at pH of 8.5. When pH $> 7.5$–8, hydrolysis of zinc goes on, and at pH of 10, Zn(OH)$_2$ reaches its maximum of 95–97%. When pH exceeds 10, dissoluble anionic zinc hydro-complexes Zn(OH)$_3^-$ are being formed [3]. This means that the optimum pH in water treatment by adsorption at manganese ore to reach the sanitary standard in terms of the toxicant is in the range of 6–10.

During Zn adsorption at manganese ore, pH of the treated water rises from 6.1 to 7.3 and to 8 in contact with Durnovskoe and Usa ore, respectively. Higher alkalinity of Usa ore samples can be explained by the higher presence of CaCO$_3$.

The value of pH has influence not only on the forms of metal in water but also on the behavior of the adsorption sites on the sorbents. As pH is decreased, the negatively charged surface sites for cation adsorption diminish in number. Iron oxides/hydroxides have a point of zero charge (PZC) in the range of pH of 7–10, i.e. play no any part on the cation adsorption at low pH as these surfaces have a positive charge in such conditions. Manganese oxides have PZC inside the range of 2.8–4.5; for this reason, at pH higher than 4.5, Mn oxide changes its surface charge to negative, which is important for
the cation adsorption. Calcite which is the main mineral of Usa ore can play an important role in zinc adsorption. For many metals (Cd, Mn, Zn, Co), absorption by lime soil was higher with calcite than without it. PZC of calcium carbonates varies between pH of 7 and 10 and depends on the type and crystallinity of a mineral [11].

The scanning electron microscopy and energy dispersive x-ray spectroscopy of the ore samples after Zn adsorption show that Zn spreads over the whole surface of the samples from both deposits, i.e. adsorption takes place both at Fe an Mn phases and at calcium carbonates.

3. Conclusions
1. The implemented research has proved usability of manganese ore from the Kemerovo Region as zinc sorbents in integrated waste water treatment.
2. Mathematically and at high correlation factor, the process of adsorption is described by the Langmuir equation which determines the quantitative characteristics of adsorption: the equilibrium constant for adsorption, the maximal adsorption capacity and the Gibbs energy change.
3. Out of two test deposits, Usa ore exhibits higher chemical affinity toward zinc.
4. Acid-base balance of water phase has a considerable influence on adsorption efficiency.

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