

Removal of metals from water using Slovakite adsorbent

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ABSTRACT

The purpose of this article is removal of copper, nickel, chromium and zinc from their model solution by precipitation and adsorption processes where metal ions are adsorbed onto the surface of materials. Inorganic granular material (Slovakite) with high content of $\text{MgO} \cdot \text{CaCO}_3$ was used in this study. Slovakite proved to be efficient for copper, nickel and chromium removal. Langmuir's and Freundlich's isotherm models adequately describe adsorption process from aqueous solution. Removal efficiency of metals, rate of metal removal and bond strength between Slovakite and metal was investigated. Slovakite is an alkaline adsorbent; therefore, pH value increases with concentration of Slovakite in solution. On this account, efficiency of metal removal depends not only on adsorption processes but also on precipitation processes.

Keywords: copper; nickel; chromium; zinc; adsorption; Slovakite

INTRODUCTION

Generally, the pollution of water is one of significant ecological problems. Among components of water pollution belong heavy metals. Heavy metals are omnipresent in environment. Their presence in the environment has become a major threat for plant, animal and human life due to their bioaccumulating tendency and toxicity. Therefore they must be removed from municipal and industrial effluents before discharge into the surface water¹. The metals may occur in the form of simple or complex cations and anions, in the form of neutral molecules (e.g. complexes with humic materials). The toxicity is mainly depending on form occurrence of appropriate metal. It stands to reason, that the essential higher toxicity belongs to ion form of metal than complex form².

The highest limiting value is for copper 1000 $\mu\text{g/L}$, nickel 20 $\mu\text{g/L}$, chromium 50 $\mu\text{g/L}$ in drinking water, but zinc is not limited (not even in packaged waters, The decree No. 252/2004 Code³).

Adsorption metals on Slovakite

Slovakite is an inorganic sorbent, which removes heavy metals ions from waste water. It has no hygienic certificate for drinking water, therefore it is used mainly for wastewater purification. Slovakite is used in powdery or granulated form and its main composition are either thermally modified dolomites with high content of $\text{MgO} \cdot \text{CaCO}_3$ and filler pasta, most often cement. This mixture has high adsorptive efficiency and is chemically stable. Slovakite sorbent has adsorption and chemisorption capabilities and other mechanisms (e.g. precipitation) how to capture cations of heavy metals. The efficiency of sorbent depends on pH of media. Content of semi-burned dolomite $\text{MgO} \cdot \text{CaCO}_3$ causes pH increase and concurrently adsorption process also begins eventually chemical adsorption on the surface grains of Slovakite⁴.

EXPERIMENTAL

The purpose of this study was observation of adsorption mechanism of copper, zinc, nickel and chromium on tested Slovakite adsorbent using Langmuir's or Freundlich's isotherm, further evaluation of process efficiency

and determination of adsorbent capacities (expressed in mg of metal per g of sorbent). Model water (tap water) was used for measurement, in which the content of metals has been artificially increased by addition of solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to concentration 100 mg/L. Weighted portions of adsorbent were chosen: 0.125g, 0.25g, 0.5g, 0.75g, 1.0g, 2.5g, 3.75g and 5g per 1L solution of appropriate metal. Because equilibrium concentration of metals was achieved approximately in 3 hours (for copper only in 1 hour), the contact time 24 hours was chosen. Contact adsorbent with solution of metal and mixing were made on shaker at rotation speed of 200 rotations per minute. For filtration was used filter paper Filtrak N₀ 389 Ø - yellow ribbon.

Evaluation of tests was made by specific adsorption and its resulting removal efficiency of metals. Specific adsorption a is quantity of adsorbed material in milligrammes per 1g of sorbent. Relation for a calculation is given by formula (1).

$$a = \frac{V}{m_s} \cdot (c_o - c_r) \quad (1)$$

where, V is initial volume of adsorption solution in litres, c_o and c_r are initial and equilibrium concentration of metal in mg/L, m_s is sorbent weight used in grams.

Removal efficiency of metal E in % for static test is determined from relation⁵:

$$E = \frac{c_o - c_r}{c_o} \cdot 100 \quad (2)$$

Freundlich's or Langmuir's isotherms are used in aquatic media mostly. Mathematical data processing with using of linear or nonlinear regression relations decides which isotherm means adsorption mechanism is the best.

Especially, Freundlich's isotherm is used for adsorption from aquatic solution during simultaneous tests of physical adsorption and adsorption on heterogenic surface with various active places, also known as multilayer adsorption. Empiric expression of Freundlich's isotherm is:

$$a = K \cdot c_r^{1/n} \quad (3)$$

where, K and n are constants and c_r is equilibrium concentration. Regarding

Freundlich's isotherm assessment, the linearization is applied with logarithmic calculation of empiric formula. Therefore, $\log a = \log K + (1/n) \cdot \log c_r$, is valid, when on horizontal axis is $\log c_r$ and on vertical one is $\log a$. We obtain K and n constants for calculation $K = 10^q$ and $n = z^{-1}$, where q and z are constants in regression line $Y = zX + q$ (q is the section and z gradient of line). The value of K constant declines when temperature increases and n is always higher than 1.

Langmuir's isotherm usually refers to chemical or electrostatic adsorption producing only one layer of adsorbate onto surface of adsorbent with constant surface properties. The Langmuir's relation has form:

$$a = \frac{a_m \cdot b \cdot c_r}{1 + b \cdot c_r}, \quad (4)$$

where, a_m and b are constants. For low concentration substance we ignore the term $1 + b \cdot c_r$ and then the above mentioned formula is simplified down to linear form $a = a_m \cdot b \cdot c_r$. However, in the case of high concentration of substance, the surface of sorbent is fully saturated and quantity adsorbed material is equal to maximum quantity $a = a_m$.

Langmuir's isotherm is interpreted in two ways:

1. On x - axis (horizontal) is c_r and on y - axis (vertical) is c_r/a . Constants a_m and b are determined from general formula of line $Y = zX + q$ and can be verified by calculation $a_m = 1/z$ and $b = 1/a_m \cdot q$.

2. On x - axis (horizontal) is $1/c_r$ and on y - axis (vertical) is $1/a$. Constants a_m and b are determined from general formula of line $Y = zX + q$ and can be verified by calculation $a_m = 1/q$ and $b = 1/a_m \cdot z$.

We also obtain regression coefficients R^2 by mathematical processing of experimental date. The closer the value R^2 to 1, the better plotting points suit for linear relation and the mechanism of adsorption is possible to be described by this one isotherm.

RESULTS AND DISCUSSION

Constants of Langmuir's and Freundlich's isotherm for individual metals are summarized in Table I. Adsorbent isotherms of these metals are given in Figure 1.

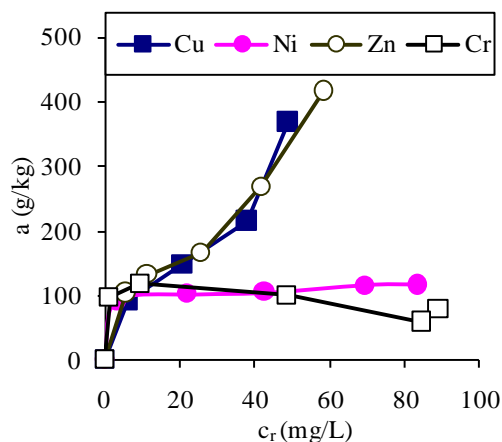


Figure 1 Adsorbent isotherm of Cu, Ni, Cr and Zn on Slovakite

Table I Constants of Langmuir and Freundlich isotherm for Cu, Ni, Cr, Zn

	Cu	Ni	Cr	Zn
a_m (mg/g)	556	120	75.2	476
b (L/mg)	0.0235	0.252	0.213	0.0425
n (-)	1.42	2.91	8.93	1.59
K (L/g)	20.2	30.0	41.8	27.8

Table II Regression coefficients R^2 of Langmuir and Freundlich isotherm for Cu, Ni, Cr, Zn

	Cu	Ni	Cr	Zn
R^2	-	-	-	-
Langmuir	0.643	0.998	0.914	0.762
R^2	-	-	-	-
Freundlich	0.945	0.783	0.0633	0.962

From Table I and Figure 1, it can be seen, that value of maximum adsorbed quantity declines in the row of Cu > Zn > Ni > Cr, whereas value for Zn and Cu is comparable and approaches 500mg/g. Values for Ni and Cr are approximately five times lower. Mechanism of adsorption of copper and zinc can be better described by Freundlich's isotherm, because regression coefficients R^2 , situated in Table II, are higher. Therefore adsorption mechanism for nickel and chromium should be described by Langmuir's isotherm.

It is clear, that removal efficiency of metals depends on concentration of adsorbent. This dependence is illustrated in Figure 2. Initial concentration of solutions were 100mg/L metal.

If we compare removal efficiency e.g. for concentration of adsorbent 0.5g/L, the value of removal efficiency for Cu and Zn is about 25% higher than Ni and Cr. Maximum removal efficiency of metals varies around 94- 99%.

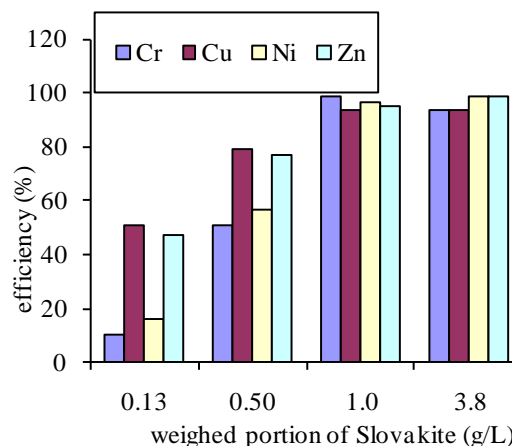


Figure 2 Dependence of metal removal efficiency on Slovakite concentration

Table III Equilibrium pH value of the solution for different weighed portion of Slovakite for Nickel (initial pH value was 7.3)

m_s (g/L)	0.13	0.5	1	3.8
pH (equilibrium)	6.8	7.2	7.6	8.2

In table III it is illustrated, how to change equilibrium pH value for different weighed portion of Slovakite. I chose nickel as an example. Precipitation contributes to the removal of nickel from value of pH = 7.6, it means for doses 1 g/L and 3.8 g/L. It was removed probably 7% of nickel by precipitation and 90% by adsorption for dose 1 g/L and 39% by precipitation and 60% by adsorption for dose 3.8 g/L (this follows from the nickel precipitation curve, but correct value should be determined by a detailed analysis of used adsorbent. There are different values for Cu, Zn and Cr because they have different precipitation curves).

CONCLUSIONS

Slovakite is suitable material for removal of heavy metals from water. Adsorbent concentration higher than 1g/L provides almost constant removal efficiencies of metals. This efficiency varies around 94%. Maximum

adsorbed quantity values decline in the following sequence of $\text{Cu} > \text{Zn} > \text{Ni} > \text{Cr}$. Mechanism of adsorption is possible to describe in the case of copper and zinc by Freundlich's isotherm and for nickel and chromium by Langmuir's one. The reasons for better removal efficiency of metals from waste water are caused not only by higher dose of Slovakite and higher equilibrium pH value, but it is also caused by the process of precipitation.

Acknowledgment

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