

The adsorption of Pb^{+II} , Cu^{+II} and Cr^{+III} on ferro-precipitate

Roman MARŠÁLEK

Department of chemistry, Faculty of science, University of Ostrava
30. dubna 22, Ostrava, Czech republic

Abstract. The main aim of the paper is to evaluate ferro-precipitate as immobilization agent for removing heavy metals from aqueous solutions. Lead, copper and chromium were used as model metals. The simultaneous measurements of the heavy metals adsorption and zeta potential determination of the (adsorption) suspensions were carried out. The adsorption isotherms were found to be of typical Langmuir type; values of the heavy metals adsorption capacities have been calculated ($a_m = 0.76 \text{ mmol g}^{-1}$ for lead, 0.58 mmol g^{-1} for copper, 0.38 mmol g^{-1} for chromium, respectively). Shape of the adsorption isotherms was correlated with zeta potential values at the adsorption equilibrium. Addition of the heavy metals ions affects the value of ξ - potential, making the zeta potential values more positive.

Keywords: ferro-precipitate; adsorption; heavy metals; zeta potential

1. Introduction

Heavy metals in waste water cause a serious environmental problem. Recently, efforts have occurred to eliminate the content of heavy metals by means of adsorption on various types of adsorption materials. Apart from the most common active coal, also cheaper options are analyzed. The following natural materials are used – various kinds of coal (lignite coals, charcoal, brown coal, bituminous coal), humic acids, peat, algae, woolen or rice materials. [1-5] The second category are waste materials, e.g. various kinds of sludge. Other interesting adsorbents offering good prospects are as well ferro-compounds such as goethite, hematite, magnetite and others. [6-10] These compounds are very often artificially synthesized and used as nano-adsorbents. These oxo ferro-compounds as well arise as waste products in particular manufacturing processes, e.g.

In the company Bochemie (Czech Republic), zinc chloride is manufactured particularly from recycled acid, which represents waste from zinc works. The problem of this production is the thick and almost unsettling sediment of iron which, moreover, retains rather big amounts of zinc chloride. The sludge consists of approximately one third of water, one third of zinc chloride and the rest are ferro-compounds. Due to the presence of zinc chloride, the sludge cannot be used to charge a blast furnace. The solution is to find a suitable process of precipitating iron in solutions, e.g. using the goethite process. The goethite process is successfully used in the electrolytic galvanization industry to turn the iron in a solution (mostly sulfide or chloride) into a sediment which is easy to filtrate. [11-12] The Electrolytic Zinc Company of Australasia developed a continuous process, during which all ferrous ions in a solution are at first oxidized, and subsequently the solution continuously flows into a reactor at a speed which eliminates the solid phase. [13]

This method was also used to precipitate iron from the waste acid used to produce zinc chloride in the company Bochemie. The process was carried out under varied conditions (temperature, pH) and resulted in sediments with varied composition and texture parameters. Sediments high in zinc, further use of which is

rather limited, were analyzed with regard to their possible use as sorbents to eliminate heavy metals from aqueous solutions.

The main goal of this study is to judge waste materials on the basis of ferrous oxide as adsorption material to eliminate ions of selected heavy metals from solutions. Further goals were to describe the adsorption process by means of some adsorption theory (Langmuir, Freundlich) and to calculate the adsorption capacity of the sorbent. By means of the zeta potential, changes on the surface of adsorption particles were monitored during the adsorption process.

2. Experimental methods

2.1. “Goethite” process

A continuous flow reactor was used in this process. 800 g of zinc chloride solution was put into a reaction vessel (filtering flask). The solution had been prepared by dissolving 240 g of solid zinc chloride in 560 g of distilled water. Recycled acid was rid of solid impurities by filtering it over a textile filter. Subsequently, all ferrous ions were oxidized into ferric ions by slowly adding hydrogen peroxide (30 %) and continuously stirring the substance. Occasional checks were carried out to find out whether all the iron had oxidized. The discharge of oxidized acid into the reaction vessel was set on a peristaltic pump. A pH electrode, a stirrer and hoses from both pumps (with oxidized recycled acid and a zinc oxide suspension) were immersed into the reaction vessel. The stirrer was switched on. After having reached the desired temperature 80 °C and pH = 2.2, both pumps and a computer program for pH were switched on. This way, the experiment began. The experiment finished after three hours.

2.2. Adsorbent

The content of iron and zinc in the sediment created by the above mentioned process was determined. Surface area (BET) was as well determined and the sample was observed by RTG diffraction. Results are summarized in table 1.

Table 1: Proximate analyses, surface area and mineral composition

Fe	Zn	S ^{BET}	RTG diffraction
%	%	m ² /g	
55.2	7.4	220.45	ferrihydrite + ferroxihite

Surface area of the sample from the adsorption isotherm of nitrogen (SBET) was evaluated according to the BET theory, using a nitrogen molecular area of 0.162 nm² for the calculation.

The normal powder XRD patterns were recorded between 5.0° and 50.0° 2 θ using CuK α 1 radiation with an INEL CPS 120 diffractometer equipped with a curved position-sensitive detector, transmission mode with the germanium monochromator.

Metal concentrations were determined by means of the ICP optical emission spectrometry (Perkin-Elmer Optima 3000 spectrometer).

2.3. Chemicals

The chemical used in this study was zinc chloride, zinc oxide, hydrogen peroxide, lead nitrate, copper nitrate and chromium nitrate. All the solutions were made in distilled water. Analytical grade chemicals were used.

2.4. Batch experiments

About 0.2 g of dried sample was added to 50 mL of a given metal solutions of known concentration varying in the range 10 - 0.1 mmol/l and occasionally shaken. Adsorption equilibration took about 3 days, as deduced from previous measurements. The zeta potential of the adsorption suspensions was measured. Then, the sample was removed by filtering through paper filter. The metal concentration of the filtered solutions was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The amount of metal adsorbed (a) was determined from the change in the solution concentration before and after equilibrium, according to:

$$a = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where c_0 is the initial concentration of metal solution, c_e the concentration of metal solution at the adsorption equilibrium, V the volume of metal solution and m the mass of the sample.

2.5. Zeta potential measurements

Zeta potential measurements was performed by analyzing 0.2 g of coal in 50 ml metal solution using the Coulter Delsa 440 SX (Coulter Electronic, USA). Delsa 440 SX uses the scattering effect of Doppler light to determine the electrophoretic mobility. The zeta potential was obtained from the electrophoretic mobility by the Smoluchowski equation:

$$\zeta = \frac{\mu\eta}{\varepsilon} \quad (2)$$

ζ is the zeta potential (V), η represents dynamic viscosity (Pa.s), and ε stands for the dielectric constant. The fixed conditions of measuring were the following ones: temperature (298 K), electric field (15 V), frequency (500 Hz), and the properties of the samples – viscosity ($0.0089 \text{ kg.m}^{-1}.\text{s}^{-1}$), refraction index (1.333), and dielectric constant (78.36).

3. Results and discussion

3.1. Characterization of sample

Data from RTG diffraction show that the sample contains a significant amount of amorphous phase; the following two ferrous compounds are present - ferrihydrite $\text{Fe}_5\text{O}_7(\text{OH}).4\text{H}_2\text{O}$ (30%) and ferroxihite $\delta\text{-FeO}(\text{OH})$ (20%). The relatively high content of zinc makes disposal of this material (waste) in blast furnace impossible. This fact represents the main reason for looking for new (other) effective ways of using this material. The relatively large specific surface area contributes to using the material as adsorbent (see table 1).

3.2. Adsorption of metallic ions

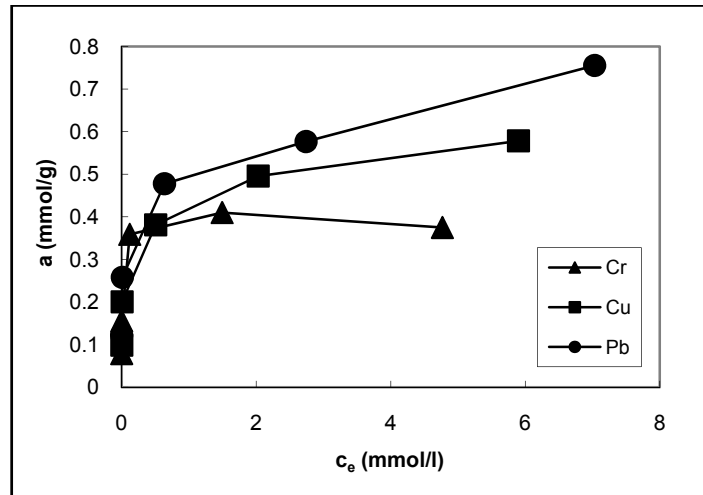


Fig 1.: Adsorption of Pb, Cu and Cr ions on ferro-precipitate

Figure 1 depicts typical adsorption isotherms obtained from the experimental data. The shape of isotherms indicates that the adsorption data could be well fitted by the Langmuir adsorption model of monolayer coverage. In a linear form, the Langmuir equation is given by

$$\frac{c_e}{a} = \frac{c_e}{a_m} + \frac{1}{a_m b} \quad (3)$$

where a is the amount of the metallic ion adsorbed, c_e is an equilibrium concentration of the metallic ion in solution, K represents a monolayer binding constant and a_m is the monolayer adsorption capacity.

All adsorption isotherms proved to be consistent with the Langmuir model as deduced from calculated r-square values close to 1 (minimal r^2 value was 0.985). The most informative parameter in the Langmuir equation is a_m , providing information on adsorbed amount at monolayer surface coverage. These values are compiled in Table 2 as found for studied samples.

From the Table 2 it is obvious that Pb^{2+} cation is immobilized in the largest extent, opposite, Cr^{3+} cation is of the lowest affinity to the sample.

Table 2: Results obtained from the Langmuir equation applied to the adsorption data

Ion	$a_m(\text{mmol/g})$	$K(\text{l/mmol})$	Equation of adsorption isotherms	r^2
Pb	0.756	4.001	$a = \frac{3.024 \cdot c_e}{1 + 4.001 \cdot c_e}$	0.985
Cu	0.584	7.112	$a = \frac{4.151 \cdot c_e}{1 + 7.112 \cdot c_e}$	0.996
Cr	0.376	46.296	$a = \frac{-17.398 \cdot c_e}{1 - 46.296 \cdot c_e}$	0.999

The Langmuir adsorption theory is based on adsorption of gases and it is not apparently valid without any differences for adsorption from the solutions. Thus, the experimentally obtained data were also analyzed in terms of non-linear regression. Four adsorption models (Langmuir, Freundlich, Langmuir-Freundlich and Temkin) were used and compared. The non-linear regression was calculated by means of OPstat program using various algorithms – genetic algorithm, simplex, and Levenberg-Marquardt algorithm. Akaic criterion was chosen to evaluate the experimental data correspondence with a given theory. The lowest value of Akaic criterion was found for Langmuir model. In other words also non-linear regression confirmed Langmuir model applicability.

3.3. Zeta potential measurements

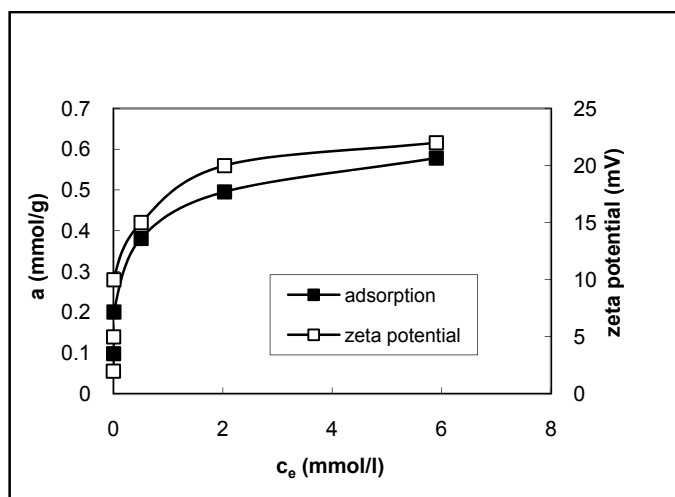


Fig. 2: Dependence of zeta potential (blank symbols) and adsorption of Cu (full symbols) on ferro-precipitate on the equilibrium concentration of the Cu solution (c_e).

Figure 2 shows the noteworthy similarity of the adsorption isotherms with the changes of zeta potential of the adsorption systems. In other words the adsorption of metal ions causes a change of the surface charge. The same results were found for other adsorption systems. [14-17].

4. Conclusions

Adsorption of selected ions of heavy metals on sediment was monitored. Apart from the amorphous phase, the sediment contained also ferrihydrite and ferroxihite. This material, which represents unusable waste, shows a relatively high adsorption capacity for heavy metal ions. The adsorption process can be described by the “classic” Langmuir theory and the calculated parameters of the Langmuir equation can be used for potential particular applications. The adsorption process was studied as well with regard to changes of surface charge. Measuring proved a connection between adsorption and the change of the zeta potential of the particles. Particularly due to its adsorption capacity and price, this material ranks among many cheap adsorption materials possibly usable to treat waste water containing heavy metals.

5. Acknowledgements

Article has been done in connection with project Institute of environmental technologies, reg. no. CZ.1.05/2.1.00/03.0100 supported by Research and Development for Innovations Operational Programme financed by Structural Funds of Europe Union and from the means of state budget of the Czech Republic and it was also supported by Ministry of Industry and Trade of the Czech Republic (FR-T11/246)..

6. References

- [1] B. Taraba and R. Marsalek. Immobilization of Heavy Metals and Phenol on Altered Bituminous Coals. *Energy Sources, Part A* . 2007, **29** (10): 885-894.
- [2] Y.H. Wang, S.H. Lin and R.S. Juang. Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents. *J Hazard Mat B*, 2003, **102** (2-3), 291-302.
- [3] M.Klucakova and L.Omelka. Sorption of metal ions on lignite and humic acid. *Chem. Pap. - Chem. Zvesti*. 2004, **58** (3): 170-175.
- [4] M. Cox, E. El-Shafey and A.A. Pichugin, Q. Appleton. Removal of mercury(II) from aqueous solution on a carbonaceous sorbent prepared from flax shive. *J Chem Technolog Biot*, 2000, **75** (6): 427-435.
- [5] A.K. Meena, G.K. Mishra, S. Kumar, Ch. Rajagopal and N.P Nagal. Low-cost adsorbents for the removal of mercury (II) from aqueous solution - A comparative study. *Defence Sci J* .2004, **54** (4): 537-548.
- [6] Y.H. Chen and F.A. Li. Kinetic study on removal of copper (II) using goethite and hematite nano-photocatalysts. *J. Colloid Interface Sci*. 2010. **347** (2): 277-281.
- [7] S. Mustafa, S. Khan and M.I. Zaman. Effect of Ni²⁺ ion doping on the physical characteristics and chromate adsorption behavior of goethite. *Water Res*. 2010. **44** (3): 918-926.
- [8] V. Campos. The sorption of toxic elements onto natural zeolite, synthetic goethite and modified powdered block carbon. *Environmental Earth Sciences*. 2009. **59** (4): 737-744.
- [9] W. Li, S.Z. Zhang and X.Q. Shan. Effect of phosphate on the adsorption of Cu and Cd on natural hematite. *Chemosphere*. 2006. **63** (8): 1235-1241.
- [10] S.R. Chowdhury and E.K. Yanful. Arsenic and chromium removal by mixed magnetite-maghemite nanoparticles and the effect of phosphate on removal. *J. Environ. Manage*. 2010. **91** (11): 2238-2247.
- [11] P.T. Davey and T.R. Scott. Removal of iron from leach liquors by the „goethite“ process, *Hydrometallurgy*, 1976, **2** (1): 25-33.
- [12] M.R.C. Ismael and J.M.R. Carvalho. Iron recovery from sulphate leach liquors in zinc hydrometallurgy, *Miner. Eng.*. 2003, **16** (1): 31-39.
- [13] P.T. Davey and T.R. Scott. Formation of β -FeOOH and α -Fe₂O₃ in the Goethite process, *Transcation of Institut Mining and Metalurgy*, 1975, Section C, pp 83–86.
- [14] A.M. Gallardo-Moreno, C.M. Gonzáles-García, M. González-Martín, M. and J.M. Bruque, J.M. Arrangement of SDS adsorbed layer on carbonaceous particles by zeta potential determinations, *Colloids Surf., A*. 2004, **249** (1-3): 57-62.
- [15] C.A. Basar, A. Karagunduz, B. Keskinler, and A. Cakici. Effect of presence of ions on surface characteristics of surfactant modified powdered activated carbon (PAC). *Appl. Surf. Sci*. 2003, **214** (1-4): 169-174.
- [16] R.S. Juang and W.L. Wu. Adsorption of sulfate and copper (II) on goethite in relation to the changes of zeta potentials. *J. Colloid Interface Sci*. 2002, **249** (1): 22-29.
- [17] R. Marsalek and Z. Navratilova. Comparative study of CTAB adsorption on bituminous coal and clay mineral. *Chem. Pap. - Chem. Zvesti.*, 2011, **65** (1): 77-84.