

DEVELOPMENT AND STUDY OF IRON-BASED NANOADSORBENTS

E. Deliyanni, D. Bakoyannakis, A. Zouboulis and K. Matis[#]

Section of Chemical Technology and Industrial Chemistry, School of Chemistry,
Aristotle University, Box 116, GR-54124 Thessaloniki, Greece

(Received 21 August 2004, accepted 15 October 2004)

Abstract

The application of an innovative, simple and low cost method was tested for the preparation of nanocrystalline iron hydroxides and oxyhydroxides; different iron precursors have been earlier used and combined to different volatile precipitating agents. The examined in the present product, akaganéite [β -FeO(OH)], had high surface area and definite pore size distribution. The produced materials were examined in detail (i.e. by powder X-ray diffraction, TEM and nitrogen sorption measurement). Main aim of this study was to evaluate the efficiency of the prepared material in the removal of heavy and toxic metal cations, like Cd(II), from aqueous solutions; cadmium constitutes a priority pollutant. Sorption was found to depended on the solution pH and its ionic strength. Typical isotherm models were applied and calculated the values of maximum adsorbent capacity for the metal as well as that of the enthalpy change during the removal process.

Keywords: akaganéite, cadmium, adsorption, wastewater

1. Introduction

The synthesis of these materials involves the hydrolysis of aqueous

[#] *Corresponding author:* kamatis@chem.auth.gr

solutions of ferric salts followed by membrane purification and freeze drying of the products [1]. Three different precursors were used and combined to three different volatile precipitating agents. The obtained products were of the following types: akaganéite [β -FeO(OH)], goethite [α -FeO(OH)] and iron(III) hydroxide. Irrespective of the starting materials used, all three products, although different in chemical nature, presented some very interesting and unique features and morphology; it was well confirmed that the obtained was a nanocrystalline material. Akaganéite, a natural oxyhydroxide mineral, has a hollandite-like (BaMnO_2) crystal structure containing tunnel-shaped cavities, running parallel to the c-axis, the sites being bound by double rows of fused octahedral in which chloride ions reside.

Various methods for its artificial synthesis have been reported [2]. This inorganic material, prepared in the laboratory, was effectively tested as an adsorbent of arsenates, occurring in many natural waters and groundwaters [3]. Adsorption isotherms were found to fit sufficiently the known Langmuir equation, with maximum sorption capacity of the order of 120 mg/g. Cost is an important parameter for comparing adsorbents and iron-based materials certainly belong to the category of low-cost ones.

Large quantities of process streams in chemical and metallurgical industries and also spent streams of hydrometallurgical origin contain rather moderate concentrations of toxic metal ions, which have to be removed or recovered, following severe environmental constraints. Cadmium-polluted wastewaters are generated by a number of industries that include mainly metal-finishing, electroplating, ceramics and inorganic pigments production, metallurgical alloying, zinc smelting, and acid mine drainage. Among the many materials been tried in the literature as Cd-sorbents the following are mentioned: zeolites, bentonite, clay, moss peat, dead biomass, chitosan, seaweed, different barks, modified wool, Turkish coffee, waste tea, nut shell, formaldehyde-polymerised peanut skin, xanthate, etc. [4]. Elsewhere, biosorption was studied in depth for cadmium ion removal; for the consequent solid/liquid separation of metal-loaded biomass flotation was applied [5].

2. Experimental

Akaganéite (denoted as Ak) was prepared in the laboratory from an

aqueous solution of iron(III) chloride salt and ammonium carbonate as precipitation agent. The crystal structure of the synthesized sample was examined by X-ray diffraction (see Fig. 1). The material that appeared in the form of powder had BET surface area of 330 m²/g (quite high) and pore sizes in the meso- and micropore regions, and also narrow pore size distribution. Its average crystallite size was 2.6 nm, estimated by TEM. Figure 2 shows a SE micrograph, which revealed that the material grains had all about similar morphology and an average size between 30-100 μm.

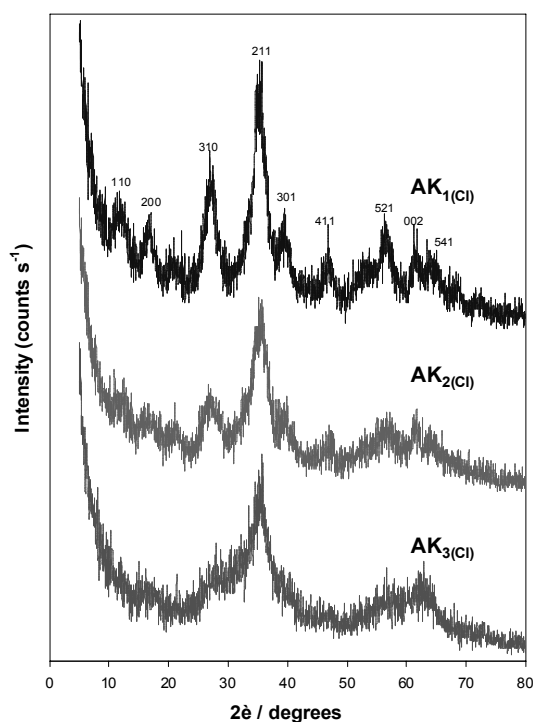


Fig. 1. XRD patterns of akaganéite and other iron oxy-hydroxide samples prepared

The experiments for toxic metal ions removal from dilute aqueous solution by the addition of this adsorbent was carried out in the present work batchwise using deionised water in suitable conical flasks being agitated with a reciprocal shaker for 24 h. The residual cadmium in solution was chemically analysed by AAS in the normal manner.

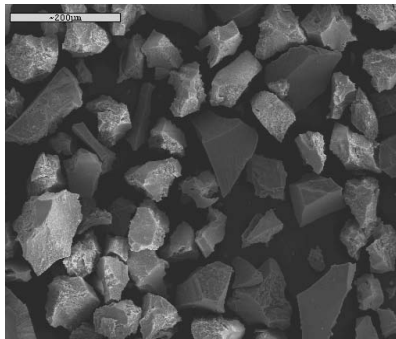


Fig. 2. SEM photograph following Cd sorption

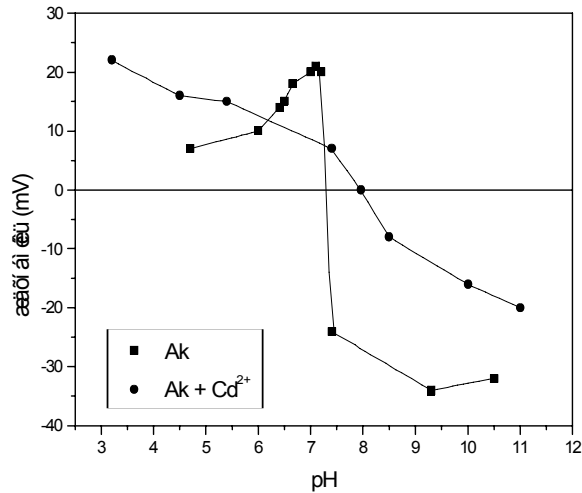


Fig. 3. Zeta-potential measurements vs. solution pH

The electrokinetic measurements are presented in Fig. 3, expressed as ζ -potential values. The point of zero charge of akaganéite after the sorption of cadmium cations was slightly shifted from 7.3 to 8 approximately – to be discussed in the following.

When one refers to cadmium sorption, not only the respective metal cation should be taken into account but also the hydrolysed metal species that exist in the solution, in relation with the pH of the solution. Hence, a thermodynamics speciation diagram (as that obtained by computer programmes like Mineql+) are usually helpful for the interpretation of experimental results [6]. It was reported, for instance, that the species responsible for sorption on oxide surfaces are CdOH^+ [7]. Nevertheless, the concentration of these ions increases at pH values greater than 8.

Freundlich model:

$$\frac{x}{m} = K_F C_{eq}^{1/n}$$

$$(K_F = 1.94, 1/n = 0.4031)$$

Langmuir model:

$$Q_{eq} = \frac{Q_{max} K_L C_{eq}}{1 + K_L C_{eq}}$$

$$(Q_{MAX} = 17.1 \text{ MG/G}, K_L = 0.0294 \text{ L/MG})$$

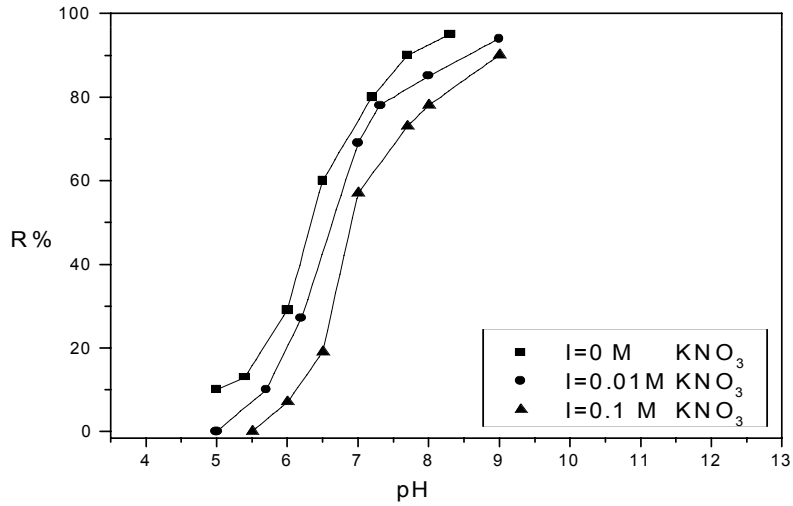


Fig. 4. Effect of pH on the adsorption of cadmium onto akaganéite, for different values of ionic strength (top)

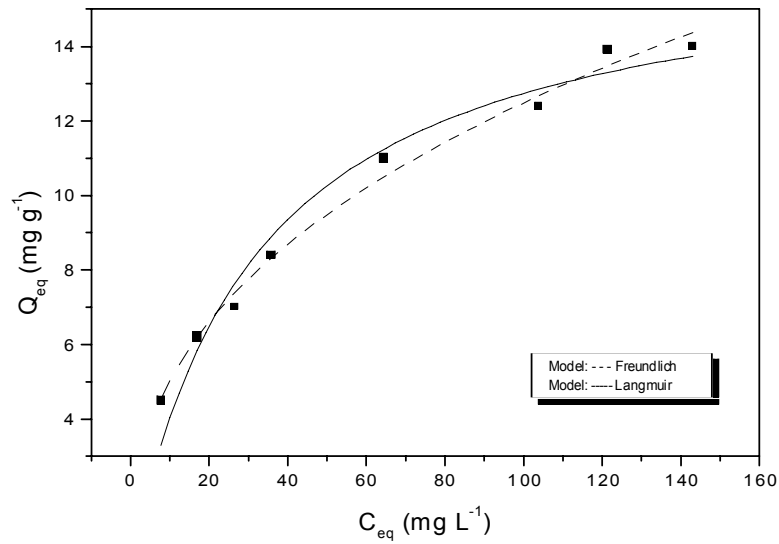


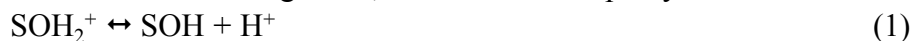
Fig. 5. Typical sorption isotherm for cadmium adsorption onto akaganéite

2. Results and Discussion

Examining the required time for cadmium removal, it was seen that although initially (from 10 mg/L Cd) there was a fast sorption of metal ions on akagenéite surface, there was the need of around 10 hours in order ~95% Cd to be removed, at pH 7; noting that this is below the region of precipitation as cadmium hydroxide. It is known that adsorption due to electrostatic forces (physical sorption) is very fast, of the order of few seconds.

The attempts to desorb the metal showed that this was possible and therefore, easy to reuse the adsorbent. Even at comparatively low pHs (around 9.5) more than 90% Cd was eluted.

The shift of the point of zero charge, described in the aforementioned, indicates a weak chemisorption or perhaps, a combination of physical and chemical sorption. In lower pH values the majority of the surface sites of the adsorbent material will be positively charged. The surface charge is due to the dissociation reactions of akaganéite, which has an ampholytic character:



where the charged surface then reacts with the electrolyte ions existing in the solution.

Testing the effect of sorbent amount, greater than 1 g/L gave constant removals. The latter was greatly affected by solution pH (Figure 4). Cadmium removals were changing from almost 0 to 95% inside a pH change of 2.5 units. In case of electrostatic adsorption, i.e. giving a possible product $(\text{SO}^-)_2 \cdots \text{Cd}^{2+}$, with the increase in pH there is a decrease of positive surface charge, hence the resistance to Coulomb forces is lowered.

From the distribution of surface species of the adsorbent it can be noticed that in this pH range there is also an increase in the concentration of surface species of SOH type (neutral); the curve of increase of SOH surface sites keeps up with that of pH change. So, the following possible reaction could be written:



in case of a surface chemisorption going on, while the species SO^- of

akagenite appear at pH greater than 8. Figure 4., also presents the influence of ionic strength of solution, showing cadmium removal to be slightly decreased with increasing ionic strength. These macroscopic observations were used to differentiate between the kind of adsorption [8].

Figure 5., shows a typical isotherm curve of 0.5 g/L material at 25 °C, I = 0. The known Langmuir and Freundlich models were then examined and both gave good fitting (with correlation coefficient, R^2 , respectively 0.994 and 0.997). From a comparison of the obtained for cadmium Q_{\max} (for a monolayer), shown also in the figure, there are cases with lower values, such as of walnut shells (1.5 mg/g) and Sphagnum moss peat (5.8 mg/g) and some of the same order, as the thermally-treated bentonite (16.5 mg/g) and zelatine (19.8 mg/g) [4]. However, there are several reports with higher capacity as given in Table 1. In general, the removal of arsenate oxyanions with the same adsorbent [3] was significantly better.

The influence of temperature was observed to give higher adsorbent capacities for cadmium (expressed as K values) with increasing it, from 25-65 °C, which indicates an endothermic phenomenon. Similar conclusions for cadmium sorption removal were also published by others [10, 12].

From the van't Hoff equation the change of the respective enthalpy was calculated and found to be $\Delta H = 25$ kcal/mol. Based on this value, it could be considered that the process mechanism is chemisorption.

4. Conclusions

In the invited plenary lecture two years ago, entitled “Mining and metallurgy: considerations of the past activity, present state and future perspectives”, given during the 34th Intl. October Conf. Mining & Metallurgy in 2002, I (KAM) referred among others to a recent review on moving from the benefits of micro to the threats of nano in the ore-mining and refining sectors [13]. The current progress in the field of recycling waste, in combination possibly with developments that make energy available in sufficient quantities at an acceptable price level, might result in technologies that isolate valuable compounds from waste at a nanoscale, thus, taking over the role of the mining industry as a provider of raw materials. It was suggested that the latter becomes involved in nanoscale research, in order to combine their knowledge

of ore properties and extraction methods with the knowledge of nanotechnological engineers about how to manipulate individual compounds.

Aim of the present paper is the investigation of nanocrystalline iron oxyhydroxides and hydroxides, synthesized in the laboratory by a novel method; various chemical reagents were tested as feed giving different products. These materials, being well characterized, have been applied to wastewater treatment in order to remove by sorption metal ions, either cations or oxyanions. The reasons for selecting these bonding materials, like goethite and akagan?ite, are that they are cheap, easily prepared and presenting low risks for adding a further pollutant to the treated aqueous system. Therefore, perhaps one may notice also our research transfer from the field of flotation, where AUTH was known, towards that of nanotechnology.

Table 1. Selected adsorbents studied for cadmium removal with the respective maximum capacity, Q_{max} (mg/g), reported.

Type	Q_{max}	Ref.
hydroxyapatite	48.8	9
actinomycetes biomass (JL & AK)	35.4, 44.4	10
zeolite	84.3	11

References

1. D.N. Bakoyannakis, E.A. Deliyanni, A.I. Zouboulis, K.A. Matis, L. Nalbandian and Th. Kehagias, *Microporous and Mesoporous Mater.*, 59 (2003) 35.
2. E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, K.A. Matis and L. Nalbandian, *Microporous and Mesoporous Mater.*, 42(2001)49.
3. E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis and K.A. Matis, *Chemosphere*, 50(2003)155.
4. S.E. Bailey, T.J. Olin, R.M. Bricka and D.D. Adrian, *Wat. Res.*, 33(1999)2469.
5. K.A. Matis, A.I. Zouboulis, A.A. Grigoriadou, N.K. Lazaridis and L.V. Ekateriniadou, *Appl. Microbiol. Biotechnol.*, 45(1996)569.

6. A.I. Zoubouls and K.A. Matis, *Wat. Sci. Tech.*, 31(3-4)(1995)315.
7. J.A. Davis and J.O. Leckie, *Envir. Sci. Tech.*, 12(1978)1309.
8. K.F. Hayes, Ch. Papelis and J.O. Leckie, *J. Coll. Interface Sci.*, 125(1988)717.
9. S. Mandjiny, A.I. Zouboulis and K.A. Matis, *Sep. Sci. Tech.*, 30(15)(1995)2963.
10. M.I. Kefala, A.I. Zouboulis and K.A. Matis, *Envir. Pollution*, 104(1999)283.
11. D. Leppert, *Mining Eng.*, 42(6)(1990)604.
12. P. Trivedi and L. Axe, *Envir. Sci. Tech.*, 35(2001)1779.
13. A.J. van Loon, *Earth-Science Rev.*, 58(2002)233.