Research of processes of lead ion sorption on bentonite clay and pectin

L V Mostalygina, S N Elizarova, A V Kostin and A G Mostalygin
Kurgan state university, Kurgan, Russia

E-mail: Mlida59@rambler.ru

Abstract. The kinetics of lead ion sorption on the pectin, excreted from vegetable objects, bentonite clay and complex sorbing agent, received on their basis, is studied. It is shown that the speed of sorption is maximum in the initial 10 minutes. The equilibration time ranges from 30 to 90 minutes, depending on the concentration of metal ions and the composition of sorbing agent. The processing of experimental sorption isotherm is made it is stated that Langmuir model suits best for the description of sorption processes.

1. Introduction

The great environmental degradation of cities in modern conditions is caused by location of numerous industrial enterprises in them, the abundance of transport and consumer waste.

In the list of substances, polluting environment most, agreed by a number of countries, there are heavy metals such as mercury, lead, cadmium and others.

Lead, not being a vital element, can cause poisoning in unfavourable conditions because of its toxicity level.

Nowadays it is stated that lead as a heavy metal binds to carboxylic, phosphate groups of biomolecules, which in its turn decreases enzyme activity and, stopping metabolic processes, causes great intoxication of the organism [1].

One of the ways out of decreasing of concentration of polluting substances is the use of sorbing agents.

The universal character of sorbing agents, which allows using them both for nonliving objects and human organism, makes them greatly attractive.

Natural sorbing agents (minerals, vegetable raw materials and etc.) have the advantage in comparison with other sorbing materials because they don’t only decrease the concentration of hazardous substances but also provide a living organism with the introduction of useful components and exclude secondary pollution of the environment.

So, the study of exchange cationic complex of Zyryansk bentonites of the Kurgan region has shown that the basic amount of exchange cations (90.17%) is accounted for by calcium and magnesium, which lets us categorize them as alkaline-earth [2].

The number of researches was devoted to the study of lead ion sorption by different forms of bentonite clays [3–6].

Pectin substances are one of the most important components of fibers, the qualities of which (cation-exchange, sorptive, chelating) determine the opportunity of their wide-spread use in the production of food both for mass market and for therapeutic purpose.
The data were received on the lead-binding capacity of pectins with different molecular mass as well [7,8].

The available information has allowed defining the possibility of the both individual and complex use of bentonite clay and pectin as sorbing agents for binding lead ions from different environments and the prospect of enterosorption as well. At the same time the study of the sorption process itself is important.

2. Methodics of study

The pectin was excreted from different kinds of vegetable raw materials: apples, carrots, beetroots (local production) and citrus crusts on Lazurievskiy’s methodology.

The bentonite clay of Zyryansk mine field of the Kurgan region was dried in the air first then crushed and for 3 hours it was brought to constant weight at the temperature of 105-110°C.

The samples of pectin (P), bentonite clay (BC), and their mixture (BC+P) at the ratio of 1:1 (in mass) of 0.5000 g were taken, then were put into conical vessels of 100 ml volumetric capacity, 50 ml of simulated solution of lead salt was added in a particular concentration and left for 24 hours at room temperature (20±2°C) with intermittent mixing. After centrifugalization aliquot part of the solution was placed into the vessel for alkalimetric testing and the residual value of lead ion content was calculated by titrimetry (immediate determination of lead with Xylenol orange) or ion metrically.

Potentiometric determination of lead ion concentration was carried out with the help of lead selective electrode of mark ХС-Pb-001 on pH-metre - ionmetre «Expert — 001-3.0», reference electrode is chloride silver.

The solution of lead salt (II) with molarity of 0.1 mol/l was made of lead nitrate Pb(NO₃)₂ (puriss.p.a). All the solutions of less concentration were prepared by the method of sequential dilution.

The adsorption capacity was defined in relation to ions Pb²⁺ in concentration intervals 2.5·10⁻³—5·10⁻⁵ mol/l.

Sorption, a (mmol/g), was calculated according to the formula:

\[ a = \frac{(C_o - C_{rel}) \cdot V_k}{m}, \]

where

- \( C_o \) - the initial concentration of lead salt in simulated solution, mol/l;
- \( C_{rel} \) - the equilibrium concentration of lead salt in the solution after the sorption on natural material, mol/l;
- \( V_k \) - the volume of simulated solution, ml (\( V_k = 50 \) ml);
- \( m \) - the mass of sample weight of sorbing agent, g (\( m = 0.5000 \) g).

The experimental error was not more than 5 %.

Simultaneously activated (a) pectin analogues (Pa) and betonite clay (BCa) were studied, as well as mixtures of sorbing agents (BCa+Pa) and (BC+P)a activated by different ways. The sorption capacity of activated analogues was studied in the same conditions.

Mechanochemical activation was carried out with the use of dry preparation of sodium hydrogen carbonate in the quantity of 1% from sample mass. The activation of mixture was fulfilled in two ways:

1) each component was activated (BCa+Pa); 2) the mixture of components was activated (BC+P)a.

3. Results

For all the studied sorbing agents the rate of lead ion sorption from the solution (\( C_o = 5 \cdot 10^{-3} \) mol/l) appeared to be maximum in the first ten minutes and comprised: for BC – 0.12 mol/l ·min, for P – 0.018 mol/l ·min, BC+P – 0.025 mol/l ·min. Then the process slowed down and in the system there was equilibrium - 40 minutes (BC), 50 minutes (BC+P) and 60 minutes (P) (figure 1).
It is stated that depending on the initial concentration of lead ions and the composition of sorbing agent, the equilibrium occurred, on average, in 30-90 minutes.

So, the rate of the sorption process is maximum on the bentonite clay and it is minimum on the pectin.

The experimental data on the efficiency of lead ion sorption by the studied sorbing agents are presented in the form of sorption isotherm (figure 2).

Bentonite clay has the highest sorption capacity. So, at the maximum studied initial concentration of lead salt – $2.5 \times 10^{-2}$ mol/l – sorption value for BC is equal to 0.59 mmol/g, for the composition of BC+P = 1:1 – 0.44 mmol/g, for P – 0.31 mmol/g.

It turned out that activated sorbing agents, on average, show sorption values (degree of absorption) of lead ion that are higher by 1.26 times in comparison with those, shown by non-activated and, moreover, preliminary activation of each component increases sorption capacity in a greater degree in comparison with the activation of the composition (on average, by 6–8%).

The study of sorption character showed that in the zone of low concentration of lead ions (II), and up to minimum that was studied - $5 \times 10^{-4}$ mol/l, the values of sorption capacity are quite close. While increasing the concentration of the solution, the difference in sorption rises.

The experimental sorption isotherms are processed mathematically: with the models of Langmuir and Freundlich. Real values of empirical constants of equations of Freundlich and Langmuir and coefficients of correlation are calculated (table 1).

**Table 1.** Description of sorption processes with the use of Langmuir and Freundlich models.

| System                      | $A_\infty$ | $K$  | $r$  |
|-----------------------------|------------|------|------|
| solution Pb(NO₃)₂ – BC      | 0.63       | 3.7  | 0.92 |
| solution Pb(NO₃)₂ – P       | 0.64       | 4.71 | 0.99 |
| solution Pb(NO₃)₂ – BC + P (1:1) | 0.64       | 7.56 | 0.99 |

| System                      | $k$    | $n$    | $r$  |
|-----------------------------|--------|--------|------|
| solution Pb(NO₃)₂ – BC      | 0.4231 | 1.7513 | 0.90 |
| solution Pb(NO₃)₂ – P       | 1.8103 | 1.6333 | 0.96 |
| solution Pb(NO₃)₂ – BC + P (1:1) | 1.6242 | 1.5423 | 0.98 |

**Figure 1.** Dependence of adsorption value on contact time of lead salt solution (II) ($C_0 = 5 \times 10^{-3}$ mol/l) with natural sorbing agents: BC (clay), P (pectin), composition BC+P (1:1).

**Figure 2.** Sorption isotherm of lead ions (II) by natural sorbing agents: BC (clay), P (pectin), composition BC+P (1:1).
According to the correlation coefficients, given in table 1, it is seen that, on the whole, Langmuir model suits better for the description of sorption of sorbing agents. Though for Freundlich model in case with P and BC+P quite high values of correlation coefficients were got too. This points to fact that on the surface of the sorbing agents there are a few active centres with an equal energy, i.e. it doesn’t satisfy boundary conditions of Langmuir model validity with monomolecular coating, which can be an indirect proof of the validity of Freundlich model. According to model the adsorption tales place on the heterogenetic surface, and active centres have different values of adsorption energy.

So, pectin introduction into native bentonite clay decreases its sorption capacity. It is possible that on pectin surface functional groups produce positive charge, which compensates for surface negative charge of the clay and thus the electric attraction of cations to the surface of such complex sorbing agent is growing weaker.

In the composition of pectin molecule there can be different functional groups: hydroxylic, methyl, aceto-groups and others, notably the presence of most groups ensures negative charge on the surface (methyl, carboxymethyl and etc). This ensures cation-exchange properties of pectin. Other functional groups, for example, hydroxylic ones can bear a positive charge and bind negatively charged ions – anions. It means that pectin can be both cation- and anion-exchanger, which can’t be said about clay.

References
[1] Huang Li, Hongquing Hu, Xueyuan Li and Loretta Y Li 2010 Influence of low molar mass organic acids on the adsorbtion of Cd$^{2+}$ and Pb$^{2+}$ by goethite and montmorillonite Appl. Clay Sci. 49 281-7
[2] Mashchenko Yu A 2003 Bentonite clays Bull. of higher educational institutions Mountain magazine 4 47–52
[3] Jiang Q, Wang X, Jin Z and Chen M 2009 Removal of Pb(II) from aqueous solution using modified and unmodified kaolinite clay J. of hazardous materials 170 332–9
[4] Kostin A V, Mostalygina L V and Bukhtoyarov O I 2012 Study of the mechanism of sorption of ions of copper and lead in bentonite clay Sorption and chromatographic processes 12(6) 949-57
[5] Elizarova S N, Mostalygina L V and Kostin A V 2014 Comparative analysis of sorption of lead ions by fibers and bentonite clays of the Kurgan Region Bull. of Moscow state pedagogical university Series: Natural sciences 2(14) 47-54
[6] Vezentsev A I, Goldovskaya L F, Volovicheva N A and Korolkova S V 2008 Research of efficiency of ion sorption Cu(II) and Pb(II) by native forms of montmorillonite clays of the Belgorod region Sorption and chromatographic processes 8(5) 807-11
[7] Makarova K E, Khozhainenko E V, Khotimenko R Yu and Kovalev V V 2013 Comparative lead binding activity of pectins with different molecular mass IN VITRO Pacific medical magazine 2 85-8
[8] Vasilenko Yu K, Moskalenko S V and Kiyschcheva N Sh 1997 Gaining and studying physical chemical and hepatoprotective qualities of pectin substances Chemical-pharmaceutical magazine 31(6) 28-9