The Removal of Heavy Metal lons by Synthetic Zeolites: A Review

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A The Removal of Heavy Metal lons by Synthetic Zeolites: Sorption techniques are widely used to remove heavy metal ions from large volumes of aqueous solutions. Herein, the synthetic zeolites, are reviewed as adsorbents in the removal of different heavy metal ions, such as Cu(II), Pb(II), Cd(II), Zn(II), Cr(III), Ni(II), Co(III), Mn(II) from large volumes of aqueous solutions. The sorption kinetics, thermodynamics and the influence of different factors on the sorption, the possible sorption mechanism of heavy metal ions and the modification of adsorbents on the removal of heavy metal ions are discussed. Different models for the simulation of sorption isotherms and kinetic sorption data are given as a comparison to understand the sorption mechanism.

Key words: Sorption, Models, Kinetic, Heavy Metal ions, Synthetic zeolites, Thermodynamic.

INTRODUCTION

The use of synthetic zeolites as sorbents on modern industry, agriculture and environment protection has been reported in the literature. Synthetic zeolites are very promising and suitable for such purposes due to their porous structure. The main advantages of the synthetic zeolites are the high phase purity, selecgivity of the ion exchange, good resistance to chemical agents and excellent thermal stability.

Water pollution with heavy metals and their purification acquires increasing importance for the development of modern industry, the issue is relevant and important to global pollution.

The heavy metal ions are toxic to living organisms. These metal ions are nondegradable and are persistent in the environment. Therefore, the elimination of heavy metal ions from wastewater is important to protect public health. Sorption is considered as a very effective and economical process for metal ion removal from wastewaters. Up to now, plenty of research work has been focused on the sorption kinetics and thermodynamics, the factors influencing sorption properties, the possible sorption mechanisms and the modification of the adsorbents. In this review, we summarized the sorption kinetics and thermodynamics, sorption isotherm models, some mechanisms of metal ion sorption on different kinds of synthetic zeolites in the recent studies.

An important feature of the adsorption of ions in zeolites and an exchange adsorption phenomenon. Its essence is as follows: when an ion adsorption on the surface of an adsorbent is caused neutrality violation of the adsorbent as a whole. This disorder is compensated by sending an ion with the same charge of adsorbent in the solution. Natural and synthetic zeolites are low-cost ion exchange and sorption materials. Ion exchange of zeolite are relatively harmless and that makes them very attractive as materials for the separation of undesirable ions of heavy metals from industrial and technological waste.

Sorption of heavy metal ions

This study follows the issues explore options for the treatment of aqueous solutions containing ions of heavy metals, synthetic zeolites using the methods of adsorption and ion exchange. Higher levels of heavy metals in aquatic facilities pose a major risk to human health. It is therefore important to find ways to abate or remove such pollutants from ponds used for drinking water [1]. For this purpose more clay minerals, activated carbon, biosorbents, metal oxides used [2,3].

The distribution of heavy metals on human health can be seen in Table 1. According to the degree of danger formed three groups, the first group includes metals with high risk.

Half-life period of cadmium in the soil was 110 years, zinc has 150 years, the copper than in 1000 years, and lead between 2-3 thousand years, depending on their ion exchange.

Groups	Heavy metals	
First group	Mercury, Cadmium, Lead, Arsenic, Selenium, Zinc, Titanium	
Second group	Cobalt, Nickel, Molybdenum, Copper, Chromium	
Third group	Barium, Vanadium, Manganese, Strontium, Aluminum	

Table 1. Heavy metal groups according to the degree of risk

By Fig.1 we can see that the exchange of heavy metals in the environment is very intense and covers all aspects of the environment. Limiting the impact of metals weigh the various environmental factors is complex and very difficult to solve practical problem.



Fig.1 Circle of heavy metals in nature

Fig. 2 shows us the way of toxicity to humans. From this it appears that the toxicity of the human body is mainly done by three factors of the environment - atmosphere, hydrosphere, and indirectly through food - lithosphere. Of these three factors hydrosphere is widest because the composition of the environment hydrosphere occupied 70.8% of the Earth's surface [3].



Fig. 2. Path of toxicity of the human body

The process of adsorption is now widely accepted, very effective and economically viable to be used to remove heavy metal ions, molecules or gases in industrial waste as well as in drinking water. The use of zeolites for this purpose is practiced very often because it is possible for precision process, selective adsorption and regeneration methods. These are some of the unique properties of zeolites makes them adsorbents for the future. That the efforts of many researchers have focused in this direction.

Zeolites are hydrated aluminosilicates of alkali and alkaline earth elements with unique crystal structures consisting of a three-dimensional framework of SiO₄ and AlO₄ tetrahedral. This structure causes zeolite to have negatively charged surface which can be used for adsorption of metals.

Several researchers have studied the removal performance and selectivity sequence of heavy metal ions by natural zeolites (Ouki and Kavannagh, 1997; Singh *et al.*, 2000; Inglezakis *et al.*, 2002, 2003; Panayotova and Velikov, 2003) [4-7] as well as synthetic zeolites (Moreno *et al.*, 2001; Querol *et al.*, 2002; Alvarez-Ayuso *et al.*, 2003) [7-9]. Ouki and Kavannagh (1997) studied the performance of natural zeolites (clinoptilolite

and chabazite) on the treatment of mixed metal effluents {Pb(II), Cd(II), Cu(II), Zn(II), Cr(III) and Co(II), the adsorption of such metals was found to be a pseudo-first-order kinetic reaction (Panayotova and Velikov, 2003) [7]. Alvarez-Ayuso et al. (2003)[9] studied the sorption behavior of Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) ions by natural (clinoptilolite) and synthetic (NaP1) zeolites. They found that the sorption capacity of synthetic NaP1 zeolite was 10 times greater than the natural zeolite. Babel and Kurniawan (2003) [10] studied Cr(VI) uptake from simulated wastewater using natural zeolite. NaCl treated zeolite had better removal capabilities (3.23 mg g^{-1}) for Cr(VI) ions than as-received zeolite (1.79 mg g^{-1}) at an initial Cr concentration of 20 mg L⁻¹. These results suggest that the Cr(VI) adsorption capacities by zeolite varied, depending on the extent of chemical treatment (Wingenfelder et al., 2005) [11]. The results were significantly lower than those of Peric et al. (2004), who also used zeolite for Zn(II) and Cu(II) removal. Zamzow and Murphy (1992) and Later, Colella et al. (1998) investigated the removal capacity of a wide variety of zeolite minerals for cadmium, copper and zinc. They revealed that zinc had the lowest adsorbed ions, among others, by all types of zeolites. Trgo and Peric (2003) [12] recommended the use of zeolite tuff as an ion exchanger in the technological processes of water with low Zn ion concentrations. Oren and Kaya (2006) [13] investigated the efficiency of two natural zeolites from Turkey, which consist mainly of clinoptilolite, in the removal of zinc ions from aqueous solutions. The adsorption behavior of both zeolites was highly dependent on the pH and the initial zinc ion concentration. The adsorption capacity of two commercial zeolites (zeolite X and clinoptilolite) had been studied by performing batch tests in Zn(II) aqueous solutions at neutral pH (Veronica et al., 2003) [14]. The results showed that zeolite surface reactivity was greatly influenced by the mineral cagelike structure and particularly the presence of pockets, spaces and channels. Georgiev et al.(2012) explore the possibility of adsorption of Cu(II), Zn(II), Cd(II) and Pb(II) ions in aqueous solutions of synthetic zeolite NaA. For this purpose, studied the effect of the environment (for Cu(II) ions, the optimum pH 3-5), initial concentrations of metal ions and the effect of contact with the adsorbent at different temperatures (298 - 328 K). The experimental research results show good agreement of different adsorption isotherms (Langmuir, Freundlich, Temkin) [15-18].

Kinetics

The real challenge in the field of adsorption is to examine and determine its kinetics, since in this way one can describe the level and the use of adsorption, which in turn will help to provide a mechanism of adsorption. Some researchers have used different kinetic models to provide a mechanism of the adsorption process. Among them the most popular are the pseudo-first order kinetics generation, pseudo-second order kinetics genus kinetic model of Weber a and Morris, sorption model Elovich, models Ritchies, Bhattacharya and Venkobachar, described in the literature (table 2)[19,20].

The utilization and accuracy of the kinetic model is usually a function of the number of independent parameters, but its popularity is related to the mathematical simplicity of the described process. Many commonly used linear regression to determine the most appropriate kinetic equation, mainly because of its usefulness in the interpretation of various data of adsorption and partly because of the simplicity of its equations. Linear method of least squares is widely used to confirm the experimental data by transoformed equations used in kinetic models. However, in recent years, the interest is related to the modeling of the development and use of nonlinear optimization. This is primarily because such a transformation of nonlinear equations in linear form leads to changes in the structure of their error and error may violate the assumptions of normality of least squares [21-26].

Nonlinear method for analyzing experimental data provides a more complex mathematical forms to determine the kinetic parameters and runs the same abscissa and ordinate, thus avoiding the drawbacks of linearization.

Kinetics models	Functional Equations	
Pseudo-first order model Lagergren model	$\frac{dq}{dt} = k(q_e - q)$	
Bhattacharya and Venkobachar model	$\frac{dq}{dt} = k_1 C - k_2 C_s$	
Pseudo-second order model	$\frac{dq}{dt} = k(q_e - q)^2$	
Elovich model	$\frac{dq}{dt} = \alpha \exp(-\beta q)$	
Adam-Bohart-Thomas model	$\frac{dq}{dt} = k_{sorp}C(q_e - q) - k_{des}q$	

Table 2. The functional Equations of different kinetics models

Table 3 reflect the functional equations of different isothermal most popular models of adsorption in literature.

Table 3. The functional Equations of different adsorption models

Izoterms	Functional Form
Freundlich	$q_e = K_F C_e^{1/n}$
Langmuir	$q_e = q_{\max} \frac{K_1 C_e}{1 + K_L C_e}$
Temkin	$q_e = \frac{RT}{b} \ln(\alpha C_e)$
Dubinin-Radushkevich	$q_e = q_{\max} \exp(-(\frac{RT \ln(C_e - C_s)}{\beta E_o})^2)$
Flory-Huggins	$\log \frac{Q}{C_o} = \log K_{FN} + n_{FN} \log(1 - Q)$
Halsey	$q_e = \left(\frac{K_H}{C_o}\right)^{1/n_H}$
Brunauer, Emmett and Teller(BET)	$q_{e} = q_{\max} \frac{BC_{o}}{q_{\max}(C_{e} - C_{o})[1 + (B - 1)(C_{e} / C_{o})]}$
Sips	$q_e = q_{\max} \frac{(K_s C_o)^{\gamma}}{(1 + (K_s C_o \gamma)^{\gamma})}$
Toth	$q_{e} = q_{\max} \frac{b_{T} C_{e}}{(1 + (b_{T} C_{e})^{n_{T}})^{1/n_{T}}}$
Redlich-Paterson	$q_e = \frac{K_{RP}C_e}{1 + \alpha_{RP}C_e^{\beta}}$

Nomenclature:

- C_e equilibrium concentration;
- $C_{\mbox{\scriptsize s}}$ adsorbate solubility at a given temperature;
- E_0 solid characteristic energy towards a reference compound; $q_c\,$ amount adsorbed;
- q_{max} saturated monolayer sorption capacity In the kinetics equations;
- q_e the amount of solute adsorbed at equilibrium;
- q the amount of solute adsorbed at any given time "t";
- C the concentrations of sorbate in solution at any given time 't';
- $C_{o}% ^{\prime}(t)=0$ the concentrations of sorbate in sorbent at any time "t".

Georgiev et al. (2012) conducted a comparative analysis between linear and nonlinear method for determining the kinetic pseudo-second order model to describe the kinetic parameters of adsorption of Cu (II) ions in aqueous solution of synthetic zeolite NaA. This study confirms that it is appropriate to use the straight non-line method for the determination of kinetic parameters of the kinetic model. This is because the transformation of nonlinear kinetics in linearized shape tends to change the distribution of the error, and thus distort the model parameters. Nonlinear analysis showed that the abscissa and ordinates results have the same error distribution and therefore it is best to obtain the kinetic parameters compared with the linear method [18,26].

CONCLUSIONS

Water pollution with heavy metals and their purification acquires increasing importance for the development of modern industry, the issue is relevant and important to global pollution. Higher levels of heavy metals in aquatic facilities pose a major risk to human health. It is therefore important to find ways to abate or remove such pollutants from ponds used for drinking water.

This study follows the issues explore options for the treatment of aqueous solutions containing ions of heavy metals, by sinthetic zeolites using the methods of adsorption and ion exchange.

The use of zeolites as sorbents are often preferred due to their specific structure, which allows the selectivity of the processes involved (adsorption and ion exchange), and relatively simple operation with them and efficiency. This is achieved as a result of the fundamental properties of synthetic zeolites, mainly as a highly developed porous surface, phase purity and resistance to chemical reagents.

A review of important publications dealing with issues of adsorption of heavy metal from aqueous solutions by zeolites.

An overview of the most used and isothermal kinetic models of adsorption and their functional equations.

Available to non-linear method is used to analyze experimental data to determine the kinetic parameters of the kinetic model, thus avoiding the drawbacks of linearization.

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