POSSIBLE USE OF METAL-MODIFIED CLINOPTILOLITE FOR CHROMIUM REMOVAL FROM WASTEWATER

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ABSTRACT. Chromium and its compounds are widely used in many industries such as metallurgy, metal finishing, production of chemicals. The effluent from these industries contain hexavalent chromium, Cr(VI), at concentrations ranging from tens to hundreds of mg/L. Different methods have been proposed for Cr(VI) removal from wastewater, such as: chemical reduction followed by precipitation, solvent extraction, ions exchange, electrochemical reduction and precipitation, membrane processes. These methods are cost intensive and are often unaffordable for large scale treatment of wastewater that is rich in Cr(VI). Zeolites are an appropriate material for removing heavy metal ions from wastewater because of their relatively low price coupled with the harmlessness of their exchangeable ions. Natural and metal modified - with Cu (II), Fe(II), Fe(III) and Pb(II) - Bulgarian zeolite clinoptilolite from East Rhodopes region has been studied for its ability to remove chromium oxyanions from model wastewater. It has been found that natural and Cu(II) - modified zeolite possesses negligible ability to uptake Cr(VI) from soft neutral model industrial wastewater. Zeolite's modification by its pre-treatment with Fe(II), Fe(III) and Pb(II) solutions increases its uptake capacity. Pb-modified zeolite removes over 95 % of available Cr(VI) in one step for 30 min at initial Cr(VI) concentration of 30 mg/L and pH=6. Over 45 % of available Cr(VI) were removed in one step for 30 min at initial Cr(VI) concentration of 10 mg/L and pH=6 by Fe(III) modified zeolite. These facts could be a basis for using this natural clinoptilolitic rock to remove in consecutive steps firstly Pb(II) or Fe(III) ions and then already loaded zeolite to be used for Cr(VI) removal. Having in mind results obtained, it can be stated that chromium removal decreases with increasing the pH value of wastewater, subjected to treatment. The zeolite uptake capacity increases with increase in pollutant's initial concentration. Kinetics of Cr uptake by Fe(II) and Fe(III) modified zeolite obeys the pseudo-first order kinetic equation for adsorption. This fact, together with the correlation that was found between Cr uptake and Na$^+$ and K$^+$ release into solution, shows the importance of ions-exchange processes in Cr immobilisation by iron-modified zeolite. Kinetics of Cr uptake by Pb-modified zeolite is described by the equation for the first order irreversible reactions. The findings support the idea for mechanism of the surface chemical precipitation of PbCrO$_4$.

Key words: zeolite, wastewater, chromium (VI)

ВЪЗМОЖНО ИЗПОЛЗВАНЕ НА КЛИНОПТИЛОЛИТ, МОДИФИЦИРАН С МЕТАЛИ, ЗА ОТСТРАНЯВАНЕ НА ХРОМ ОТ ОТПАДЪЧНИ ВОДИ
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РЕЗЮМЕ. Хромът и неговите съединения са широко използвани в много отрасли като металургия, обработване на метали, производство на химикали. Отпадъчните течни потоци от тези индустрии съдържат шествалентен хром, Cr (VI), в концентрации, вариращи от десетки до стотици mg/L. Предложени са различни методи за отстраняване на Cr (VI) от отпадъчни води, като: химична редукция, последвана от утаяване; екстракция с разтворител; йонен обмен; електрохимични процеси, директно утаяване, мембранни процеси. Тези методи са сравнително скъпи и често са икономически неефективни за пречистване на големи обеми отпадъчни води, замърсени с Cr (VI). Зеолитите са подходящ материал за отстраняване на тежки метални йони от отпадъчни води, поради тяхната относително ниска цена, съчетана с факта, че обменните им йони са безопасни. Естествен и модифициран с Cu (II), Fe(II), Fe(III) и Pb(II) български зеолит клиноптилолит от региона на Източните Родопи е изследван за способността му да отстрани хромни оксианиони от моделна отпадъчна вода. Установено е, че природният и модифицираният с Cu (II) зеолит притежава ниска способност да имобилизира Cr (VI) от мека неутрална промишлена отпадъчна вода. Модифицирането на зеолита чрез предварителното му обработване с разтвори на Fe(II), Fe(III) и Pb(II) увеличава капацитета му да задържи Cr. Зеолитът, модифициран с Pb отстранява над 95 % от първоначално наличния Cr(VI) при еднократно третиране в продължение на 30 min, при 30 mg/L начална концентрация на Cr(VI) и pH=6. Над 45 % от наличните Cr(VI) йони се отстраняват в един етап за 30 min при 10 mg/L начална концентрация на Cr(VI) и pH=6 с помощта на Fe(III)-модифициран зеолит. Тези факти могат да бъдат основа за използване на природен клиноптилолит за отстраняване в последователни стъпки първо на Pb (II) или Fe (III) йони и след това - на Cr (VI). На базата на получените резултатите може да се каже, че ефективността на отстраняването на хром намалява с увеличаване на pH стойността на отпадъчните води, подложени на третиране. Капацитетът на зеолита да имобилизира замърсителя нараства с увеличаване на първоначалната концентрация на замърсителя. Кинетика на имобилизация на Cr от зеолит, модифициран с Fe(II) и Fe(III) се подчинява на псевдо-първи порядък кинетично уравнението за адсорбция. Този факт, заедно с корелацията, намерена между задържането на Cr и изпускането на Na$^+$ и K$^+$ в разтвора, показва важността на йоно-обменните процеси в имобилизацията на Cr. Кинетика на задържане на Cr от Pb-модифициран зеолит се описва от уравнението за първи порядък за необратими реакции. Резултатите подкрепят идеята за механизъм на повърхностно химично утаяване на PbCrO$_4$.

Ключови думи: зеолит, отпадъчна вода, хром (VI)

Introduction

Many industries can be source of wastewater, polluted by chromium and its compounds, such as metals' extraction (mining, mineral processing, metallurgy); metal finishing; production of chemical compounds (dyes, chromate colour pigments, corrosion inhibition pigments, inks, certain glues); industrial use of chromium compounds (in glass and ceramics, in tanning of leather, in textile dyeing and wood preserving industries). The effluent from these industries contain

hexavalent chromium, Cr(VI), at concentrations ranging from tens to hundreds of mg/L - fortunately - most of them in the low edge of the range. Chromium (VI) is known to be more toxic to humans, animals, and plants, and more mobile in the environment than chromium (III). Water insoluble Cr(III) compounds and chromium metal are not considered a health hazard, while the toxicity, carcinogenic and mutagenic properties of Cr(VI) are well known (IARC, 1982).

Different methods have been proposed for Cr(VI) removal from wastewater, such as: chemical reduction followed by precipitation (Su and Ludwig, 2005), solvent extraction (Cooney et al., 1992), ions exchange (Rengaraj et al., 2003), electrochemical reduction and precipitation (Rayman and White, 2009), membrane processes (Alliane et al., 2001; Peng et al., 2005; Mousavi et al., 2009). These methods are cost intensive and are unaffordable for large scale treatment of wastewater that is rich in Cr(VI). Adsorption using the activated carbon is an effective and quite popular method for treating the industrial effluents polluted with Cr (VI) (Selvi et al., 2001; Leinonen and Lehto, 2001). The cost associated with use of the commercial activated carbon is very high which makes the adsorption process expensive. Cost effective alternate adsorbents for treatment of Cr(VI) contaminated waste streams are needed. Different low cost adsorbents have been studied - hazelnut shell (Cimino et al., 2000), leaves (Babu and Gupta, 2008), loamy sand soil (Fonseca et al., 2009), iron oxide coated sand (Dhagat et al., 2013).

Zeolites are an appropriate material for removing heavy metal ions from wastewater because of their relatively low price coupled with the harmlessness of their exchangeable ions. Behaviour of Greek natural zeolite-clinoptilolite towards chromium was studied with a positive result (Loizidou et al., 1992). On the other hand, it is accepted that anions were not adsorbed by the zeolites (Zamzow et al., 1990; Silva et al., 2008). In order to improve their uptake capacity for Cr(VI) species, zeolites were modified in different ways – with metal ions (Bolortamir and Egashira, 2008) and organic compounds (Warchoł et al., 2006; Leyva-Ramos et al., 2008). Chromium and Cu(II) co-removal by use of fluidized sand columns has been described (Sun et al., 2007). Metal modified zeolites (MMZs) can be obtained by two ways: a) simple ion-exchange of zeolite ions with metal ions with great affinity for the Cr (VI) oxyanions; b) formation on the zeolite of metal oxide species allowing direct adsorption and further retrieval of oxyanions (Figueiredo and Quintelas, 2014). Chromate / dichromate salts of Ag(I), Al(III), Ba(II), Fe(II) or Fe(III), Hg(II), Pb(II) and Zn(II) are insoluble, so it is expected that zeolites exchanged with these cations, would be able to immobilize Cr (VI) oxyanions.

Bulgaria is rich in zeolites. That is why, this paper is devoted to a study on the possibility to use natural and modified Bulgarian zeolite for removing Cr(VI) from industrial wastewater.

Methods and materials

Natural Bulgarian zeolitic rock from East Rhodopes region, containing mainly clinoptilolite was used. Its chemical composition was the following, in mass %: SiO_2 – 68.70, Fe_2O_3 – 2.28, TiO – 0.15, Al_2O_3 – 11.83, CaO – 2.66, MgO – 0.76,

MnO – 0.04, Na_2O – 1.60, K_2O – 4.01, P_2O_3 – 0.14, SO_3 – 0.225, ignition loss – 7.62, totalling – 100.02. Composition of zeolite was determined by means of classical silicate analysis. Cation-exchange capacity of clinoptilolite, determined as described by other authors (Kallo and Sherry, 1988), was 134.30 meq/100 g.

The zeolite was modified by placing it in contact (at solution to mass of zeolite ratio of 1 L: 50 g) with 0.1 M solutions of Cu^{2+}, Pb^{2+}, Fe^{2+}, and Fe^{3+}, obtained correspondingly by dissolving $CuCl_2.2H_2O$, $Pb(NO_3)_2$, $Fe(SO_4)_2.6H_2O$ and $FeCl_3$ (all p.a.) in distilled water. Initially suspension was stirred for 8 hours and then - left for 1 week. To prepare Fe(III)-modified zeolite, the procedure generally proposed by Du and co-authors (2012) was modified and used. The pH of the suspension of zeolite with $FeCl_3$ solution was adjusted to pH 6 by addition of 5M NaOH solution, the mixture was allowed to settle and the supernatant - removed. The solid was washed with distilled water till obtaining a negative result from qualitative reactions for determining modifying reagents in the water released after the washing. Then the modified zeolites were dried at 95 °C. Thus zeolites – CL-Cu, CL-Pb, CL-Fe(II) and CL-Fe(III) were obtained.

A stock solution containing 1000 mg/L of Cr(VI) was prepared by dissolving potassium chromate (K_2CrO_4) in distilled water. This solution was diluted with distilled water as required to obtain the solutions with concentrations of 5, 10 and 30 mg/L of Cr(VI). The average concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in natural Bulgarian water are around 70 and 27 mg/L correspondingly. In order to take into account the impact of water hardness ions, they were added to the prepared solutions as corresponding amounts of $CaCl_2$ and $Mg(NO_3)_2.6H_2O$ so as to give Ca^{2+} and Mg^{2+} correspondingly 100 and 30 mg/L. The solution pH was adjusted by adding 0.1 M HCl and 0.1 M NaOH solutions and measured by a laboratory pH meter. Concentrations of metal ions were determined with an ICP-AES analysis. Experiments were conducted batch-wise: 0.5 g of zeolite, contacting with 50 mL of Cr(VI) bearing solution, was shaken with an ESZTERGOM (Hungary) shaker (20 strokes/min, throw of 6 cm) for corresponding time.

Our previous studies (Panayotova and Hristova, 2010) showed that the ratio 100 mL of wastewater : 1 g of zeolite (volume to mass – v : m) was the optimum ratio. This ratio was used in all experiments and the zeolite particles' size was 0.09-0.325 mm (also found by previous studies as suitable one to study the impact of other process parameters). The impact of solutions' pH value on Cr(VI) uptake was investigated under the following conditions: solutions' concentration - 10 mg/L Cr(VI); contact time – 30 min and pH value of solutions to be treated: 6.0 and 4.0. The impact of initial Cr(VI) concentration on the pollutant removal was studied under the following conditions: contact time of 30 min, pH=6 and Cr(VI) concentrations – 5, 10 and 30 mg/L.

Desorption experiments were made in order to check how strongly Cr ions were immobilized by zeolite. One g of preloaded zeolite was placed in contact for 8 h with 100 mL of distilled water.

Each experimental result was obtained by averaging the data from two parallel experiments. Data obtained were processed with the aid of EXCEL computer program.

Results and discussion

Zeolite uptake, i.e. removal of Cr(VI) was calculated using the equation:

Removal, % = [(C_o-C_τ) /C_o] x 100   (1)

where C_o is the initial and $C_τ$ is the concentration of Cr(VI) at any time τ, mg/L.

Kinetics of Cr(VI) removal is presented in Figure 1. As it can be seen from the Figure, over 75 % of the Cr(VI) available were removed in 30 min. That is why contact time of 30 min was chosen in order to reveal more clear possible differences in Cr(VI) removal, due to influence of initial concentration and pH value of solution.
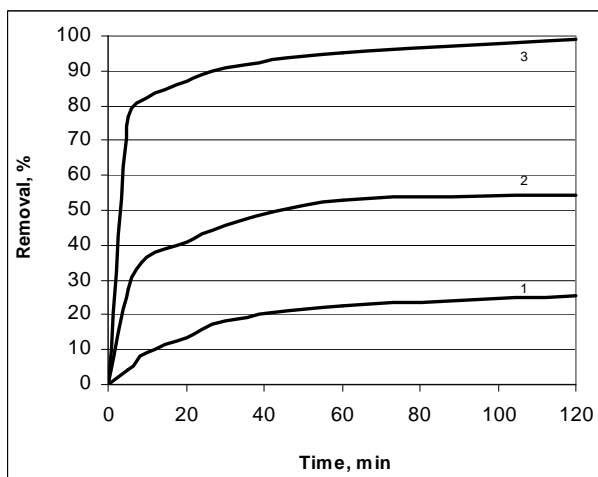

Fig. 1. Kinetic curves for Cr(VI) removal: 10 mg/L, pH = 6, v : m = 100, particles' size   0.09-0.325 mm: 1 - CL-Fe (II); 2 - CL-Fe (III); 3 - CL-Pb

As it can be seen in Figure 1, best results were observed for CL-Pb, followed by CL-Fe (III) and CL-Fe (II). Similar maximum uptake of Cr(VI) by Pb-modified zeolite, out of different MMZs was observed by other authors (Faghihian and Bowman, 2005). Most probably, the explanation lies in the formation of low soluble PbCrO$_4$. Non-meaningful results were obtained for CL-Cu and natural zeolite and for this reason they are not presented in the Figure.

Kinetic data found were fitted to different kinetic equations. Data fitting was tested in the usual way, i.e. processing the data in suitable manner and checking whether they obey the straight lines found after mathematical transformations of the corresponding kinetic equations.

For the first order irreversible reactions:

$\ln (C_o/ C_τ) = k \cdot τ$ (2)

For the second order irreversible reactions:

$(C_o - C_τ) / (C_o \cdot C_τ) = k \cdot τ$ (3)

In (2) and (3) k denotes the reaction rate constant and C_o, $C_τ$ and τ are as described above.

For the Lagergren pseudo-first order kinetic equation which usually describes adsorption of liquid / solid system, based on solid capacity:

$\log (q_e-q) = \log q_e - k_{ads} \times τ / 2.303$ (4)

where q_e, mg/g is the amount of solute adsorbed at the equilibrium; q, mg/g is the amount of solute adsorbed at time τ, k_{ads}, min^{-1} – the adsorption constant.

Equations (2), (3) and (4) were found by different authors as describing the kinetics of Cr(VI) removal.

It has been found that the kinetics of Cr(VI) removal by CL-Fe (II) and by CL-Fe (III) is best described by the pseudo-first order kinetic equation (correlation coefficient r = 0.956 and 0.995 correspondingly). A correlation (r > 0.90) was found between Cr uptake and Na$^+$ and K$^+$ release into solution for the case of CL-Fe (II) and by CL-Fe (III). This supports the idea that ions-exchange processes take part in Cr immobilisation in these cases.

Kinetics of Cr(VI) removal by CL-Pb obeys the equation for the first order irreversible reactions, with a correlation coefficient r = 0.997. This implies for different mechanisms of Cr(VI) removal - for the case of CL-Fe - by adsorption, and in the case of CL-Pb - by a chemical reaction - precipitation of PbCrO$_4$. Iron oxides-hydroxides in the case of CL-Fe(III) and PbCrO$_4$ were even visually observed on the filter paper used to separate loaded zeolite from the solution.

Results showing the impact of wastewater pH on Cr(VI) removal efficiency are presented in Table 1.

Table 1.
Impact of wastewater pH on Cr(VI) removal efficiency: 10 mg/L Cr(VI); 30 min; zeolite particles' size: 0.09-0.325 mm; v : m = 100

Type of zeolite, pH	Removal, %	
	pH =6	pH =4
Natural	0.3	2.8
CL-Cu	1.5	27.3
CL-Fe (II)	18.2	45.5
CL-Fe (III)	45.5	54.5
CL-Pb	91.3	99.1

It can be seen from the Table that Cr(VI) removal is increased at lower pH value for all types of modified zeolites, even for CL-Cu meaningful results were obtained. A trend of increase in Cr removal with pH decrease was observed by other authors (Pandey et al., 2010; Du et al., 2012; Baig et al. 2013).

Results obtained on the impact of initial Cr(VI) concentration in on removal efficiency are presented in Figure 2.

Having in mind results shown in Figure 2, it can be stated that increasing the initial pollutant concentration (in the studied range) decreases its removal, expressed as % of the initial concentration in all cases, except of - zeolite, modified with
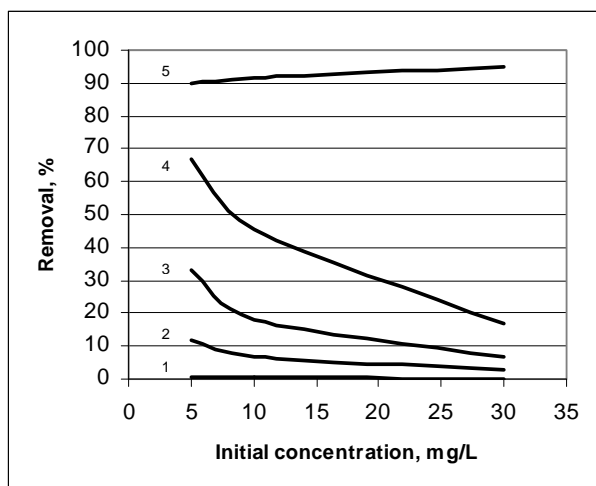
Fig 2. Impact of initial Cr(VI) concentration on removal efficiency: pH = 6; 30 min; zeolite particles' size: 0.09 - 0.325 mm; v : m = 100 : 1 - natural zeolitre; 2 - CL-Cu ; 3 - CL-Fe (II); 4 - CL-Fe (III); 5 - CL-Pb

lead, where an increase is observed. However, the uptake capacity increases with increase in initial concentration of pollutant (Figure 3).
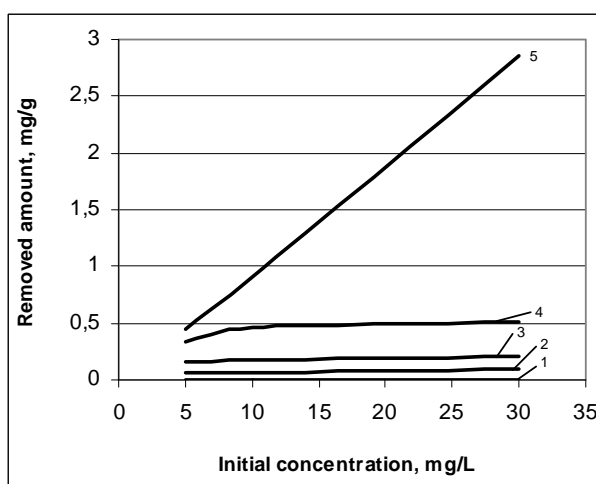

Fig 3. Impact of initial Cr(VI) concentration on the pollutant uptake, mg Cr / g zeolite: pH = 6; 30 min; zeolite particles' size: 0.09 - 0.325 mm; v : m = 100 : 1 - natural zeolitre; 2 - CL-Cu ; 3 - CL-Fe (II); 4 - CL-Fe (III); 5 - CL-Pb

Similar results were obtained by other authors (Pandey et al., 2010) in the range of 10-30 mg/L Cr. In the case of CL-Cu, CL-Fe (II) and CL-Fe (III) the result could be explained by higher driving force possessed by adsorbate at higher concentration which facilitates overcoming the mass transfer resistances of the metal ions at their movement from the aqueous to the solid phase resulting in higher probability of collision between Cr(VI) ions and the zeolite active sites. As a result higher uptake of Cr (VI) is observed. All data and results imply that in the case of CL-Pb the uptake mechanism is different from adsorption, most probably - surface precipitation. This could explain the different appearance of the line for Cr(VI) uptake by the CL-Pb. Data, presented in Figure 3, show that in the case of CL-Cu, CL-Fe (II) and CL-Fe (III) the uptake process reaches saturation (most probably when all available adsorption sites are occupied), while in the case of CL-Pb, the uptake capacity is far from reaching. This is in line with results of other authors

(Faghihian and Bowman, 2005) who obtained the uptake capacity (at equilibrium) of 29 mgCr/g zeolite, modified with Pb.

In addition it has to be recalled that it was found that Cr(VI) presenting in the wastewater can interact with Pb in wastewater forming anionic complexes, thus significantly diminishing the Pb removal efficiencies by naturally occurring Mexican clinoptilolite (Mier et al., 2001).

Results from desorption experiments showed that Cr(VI) ions were stronger immobilised by CL-Cu and weaker immobilised by the other studied types in cases when the Cr(VI) immobilization is most probably due to ions-exchange processes. About 8 % of Cr(VI) immobilised (at an initial concentration of 10 mg/L) by CL-Cu were released in the solution by zeolite contacting with distilled water. About 12 % of Cr(VI) immobilised by CL-Fe and about 10 % of Cr(VI) immobilised by CL-Fe(III) were released in the solution by zeolite contacting with distilled water. About 2 % of Cr(VI) immobilised (at an initial concentration of 30 mg/L) by CL-Pb were released in the solution by zeolite contacting with distilled water but about 10 % were released at a contact of loaded zeolite with water having pH 2, acidified with HNO_3. The probable dissolution of lead chromates under extremely acidic environmental conditions, and the toxicity associated to that compound renders this approach undesirable for environmental remediation. A feasible approach could be to use natural zeolite to remove Pb from wastewater and then to apply already loaded zeolite to remove Cr(VI). Then ether the loaded with $PbCrO_4$ zeolite should be treated as hazardous waste, or $PbCrO_4$ could be extracted as compound by zeolite contact with diluted HNO_3 and zeolite - recovered. A good compromise between performance and environmental safety can be achieved when CL-Fe (III), or eventually less toxic metal ions are used in MMZs.

Conclusions

1. Natural Bulgarian zeolite from East Rhodopes region possesses negligible ability to remove Cr(VI) from soft slightly acidic and neutral industrial wastewater.

2. Zeolite's modification by its pre-treatment with Cu(II), Fe(II) Fe(III) and Pb(II) increases its uptake capacity. Significant increase in the Cr(VI) removal was observed for lead-modified clinoptilolite. This fact could be a basis for using this natural clinoptilolitic rock to remove in consecutive steps: firstly Pb(II) and/or Fe(III) ions and then already loaded zeolite to be used for Cr(VI) removal.

3. Kinetics of Cr uptake by CL-Fe (II) and CL-Fe (III) obeys the pseudo-first order kinetic equation for adsorption. This fact, together with the correlation that was found between Cr uptake and Na^+ and K^+ release into solution, shows the importance of ions-exchange processes in Cr immobilisation.

Kinetics of Cr(VI) removal by CL-Pb obeys the equation for the first order irreversible reactions. This finding, together with other obtained facts (i.e. uptake as function of the initial Cr(VI) concentration, manner of pollutant leaching from loaded

zeolite), supports the idea for other uptake mechanism, i. e. surface chemical precipitation of $PbCrO_4$.

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