

Removal of Cr(VI) from wastewater by silver-loaded natural clinoptilolite

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Abstract. Presence of hexavalent chromium, Cr(VI), in water is an important environmental and human health problem. Natural zeolites are widely accepted as non-expensive adsorbents for sustainable remediation, however they are not effective in removing metals in anionic form. The paper presents study on use of silver (Ag) modified natural clinoptilolite to immobilize Cr(VI) ions from model and real neutral to slightly alkaline wastewater. Increasing the initial pollutant concentration increases the removed amount (80 % removal from model wastewater in 45 min at initial concentration of 30 mg Cr(VI)/L). The pseudo-second order kinetic equation best describes the Cr(VI) immobilization by the Ag-modified zeolite, which is indicative for the chemical nature of the rate-limiting step of the process. The data obtained are best fitted to the Freundlich adsorption isotherm. The Ag-modified clinoptilolite removes in 30 min over 80 % of Cr(VI), over 75 % of Cu(II) and over 70 % of Zn(II) that present simultaneously in an industrial wastewater. Due to its ability to remove Cr(VI) species, in combination with some heavy metal ions, some organic pollutants and exhibited antibacterial activity, silver loaded clinoptilolite seems to be a possible multifunctional reagent in the water and wastewater treatment and deserves further investigation.

1 Introduction

Hexavalent chromium, Cr(VI), appears in water due to natural and anthropogenic reasons. Oxidation of the chromium presenting in the igneous geologic formations is the natural source [1]. However, it is estimated that more than 70 % of Cr that is found in the environment comes from anthropogenic sources, such as nonferrous metals production (minerals beneficiation, metals smelting and refining), metals finishing and corrosion protection, paper and pulp mills, urban wastewater, etc. The effluents from these industries contain Cr(VI) at concentrations ranging from parts of the tenth to hundreds of mg/L [2]. It is established that both trivalent and hexavalent compounds of chromium are persistent in water [1]. Chromium (VI) is relatively mobile in water because its salts are more soluble than those of Cr(III) [3]. In natural waters Cr(VI) exists mainly as chromate (CrO_4^{2-}) or hydrogen chromate (HCrO_4^{2-}) ion [4].

The acute Cr intoxication via water ingestion in humans include severe gastrointestinal disorders, respiratory, liver and kidney injury, and cardiovascular collapse due to severe hypovolemia. The lethal dose is estimated at around 1 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) [5]. The exposure of human volunteers to Cr(VI) at a single dose of up to 4 mg and to Cr(III) or Cr(VI) at 5 mg in drinking water was not found to cause any adverse effect [2]. No apparent evident clinical changes or health effects were observed in humans who took Cr(VI) via drinking water at doses of between 0,03 and 4 mg per kg body weight (bw) per day for at least 3

days [2, 6]. However, gastrointestinal disorders including diarrhoea, abdominal pain, indigestion, and vomiting were associated with the chronic oral exposure of the general population in China to Cr(VI) through consumption of well water containing 20 mg Cr(VI)/L (considered to be equivalent to 0,57 mg Cr(VI)/kg bw per day). In addition, the oral exposure to Cr(VI) has been found to aggravate dermatitis of sensitive individuals [5].

Some *in vivo* studies showed that oral exposure to Cr(VI) was carcinogenic in rats and mice. The lowest-observed-adverse-effect levels in male and female rats and mice were 0,38 and 1,79 mg Cr(VI)/kg bw per day respectively [7]. Chromium (VI) shows broad genotoxicity that, together with its multispecies and multisite carcinogenicity, represents a strong evidence for a classification of Cr(VI) exposures through drinking water as probably to be carcinogenic to humans [3].

A guideline value of 50 $\mu\text{g/L}$ drinking water is proposed by WHO and the EU for total Cr on the basis of the measurability by the available analytical methods, achievability by nowadays treatment technologies, and the data from toxicology studies [4, 8]. The proposal of the European Commission is this value to be reduced to 25 $\mu\text{g/L}$ in 10 years after the new directive on the quality of water intended for human consumption will be enforced [9].

Different technologies have been applied and /or studied for removal of Cr (VI):

- Reduction coagulation filtration (RCF) - where Cr(VI) is reduced to Cr(III) by addition of ferrous salts or stannous chloride, followed by precipitation of $\text{Cr}(\text{OH})_3$,

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the latter process very often aided by addition of ferric coagulants and the final step is filtration [10.]

- Ion exchange - column strong-base or weak-base anion exchange removed 95% of the Cr(VI) ions thus achieving levels below 5 µg/L [11].

- Membrane technologies, such as nanofiltration, reverse osmosis [12] and electrodialysis [13] have been successfully tested at laboratory level for Cr(VI) removal from model wastewater.

- Microbiological removal - activated sludge has been proved at laboratory level to be effective in reducing Cr(VI) to Cr(III) and precipitating the latter within biomass. However, the microbial methods may not be suitable for drinking-water and surface water treatment as chromium removal efficiency decreased with the increase of DO and Cr(VI) initial concentration and the best results were obtained under anaerobic conditions [14].

Each of the methods described above has its own advantages and disadvantages in dependence of the Cr(VI) concentration and the presence of other pollutants resulting in inadequate removal, the high initial and/or operational costs, toxic metals sludge generation and the need of its safe disposal.

Sorption is widely accepted as a suitable method for removing pollutants presenting in relatively low concentrations in the wastewater [15]. Conventional adsorbents such as activated carbon have been widely studied for their ability to remove chromium from water [16].

Recently efforts have been placed in nanomaterials by studying and searching for low-cost and environmentally friendly adsorbents. Activated carbon -based nanocomposites, carbon nanotubes and composites based on them, and graphene-based materials have been studied for their ability to remove Cr(VI) from wastewater by sorption. Metal oxides and metals-based nanomaterials as well as polymer-based nanomaterials have also been investigated for Cr(VI) sorption [17]. However, future studies are needed to investigate the cost-effectiveness and practical applicability of the nanomaterials usage.

Natural and non-expensive adsorbents are intensively searched for in order to reduce the treatment costs and the environmental load of the adsorption process and to ensure a sustainable environmental management.

Zeolites are abundant and relatively cheap aluminosilicate materials. They are non-toxic, thermally and chemically stable - features that render them good materials for pollutants removal by adsorption processes. Their building blocks are SiO₄ or AlO₄ tetrahedral structures, connected in different ways that leads to formation of different crystalline lattice structures and ensuring high specific surface area of these materials. The isomorphic framework substitution of silicon (+4) by aluminium (+3) causes appearance of a charge deficit that is accountable for the need of charge-balancing cations, in order to keep the neutrality of the zeolitic network. Alkaline (Na⁺, K⁺) or alkaline-earth metals (Mg²⁺, Ca²⁺) are the common charge-balancing cations. The mobility of these ions ensures the ion-exchange capability of zeolites for removing cationic species from different effluents [18].

However, due to the negative charge on their surface, zeolites possess very low to negligible affinity for the exchange of anions. In order to use their excellent physical properties, combined with their low price and environmentally friendless, researchers have conducted and are carrying out many studies to tailor zeolites in order to give them the ability to remove anions [19 - 21].

Generally, the following processes have been and are being applied: i) zeolites surface modification with surfactants that ensure availability of positive charge on the zeolite surface, ii) zeolites surface modification with metal ions that form insoluble compounds with the pollutants, and iii) zeolites grafting by using molecules with affinity for negative ions [20].

While the efforts on zeolites modification with surfactants started in the 90-ties of the previous century, the studies on modification with metal ions aiming at immobilization of anions have been developed in the recent 10-15 years [22 - 26].

Faghihian and Bowman [23], who were experienced also in the zeolite modification with surfactants, stated that the metal-modified zeolite showed higher Cr(VI) uptake compared to the surfactants-modified.

In addition, the application of metal-modified zeolites exhibits an advantage of easy preparation - by simple ion-exchange process. In some cases the zeolite could be initially used to immobilize other pollutant, such as lead ions and then already loaded material to be used for removing Cr(VI) [27].

Furthermore, it would be good if the sorbent is able to simultaneously immobilize some heavy metal cations together with Cr(VI) anions - a feature that is expected to be possessed by the metal-modified zeolite if its CEC is not entirely utilized. In the treatment of water, an additional advantage would be the possible bactericidal action of the material used. Zeolite loaded with silver ions (Ag⁺), both further reduced or without reduction, showed antibacterial action against *Escherichia coli* and other microorganisms [28 - 31]. Last but not the least, silver loaded zeolite proved to be effective in the removal of an organic pollutant (xanthate) from model and clarified wastewater from flotation of zinc-lead ore [32].

The above described suggests that zeolite loaded with Ag⁺ ions could be used as a multifunctional reagent in the treatment of waters contaminated with cations, anions and organic pollutants, e.g. wastewater from various industrial activities or of groundwater intended to be brought to domestic water quality. Since the number of studies using Ag⁺-modified zeolites for removing anionic pollutants is relatively low [23, 33], in our opinion, a study on their ability to remove anions deserves the efforts.

2 Materials and methods

Natural zeolitic rock from Rhodopes region of Bulgaria was used. It was milled, the fraction 0.09-0.325 mm was separated by sieving and it was utilized in the experiments. The XRD analysis of the washed material has revealed that it contained 73% clinoptilolite. The classical silicate analysis was applied to determine the chemical composition of the material that was (in wt. %):

SiO₂ – 70,29, Al₂O₃ – 10,90, CaO – 2,97, MgO – 0,51, K₂O – 3,41, Na₂O – 0,46, Fe₂O₃ – 0,28, MnO – 0,04, TiO – 0,06, P₂O₃ < 0,05, SO₃ < 0,05, LOI – 10,99. The theoretical cation exchange capacity (TCEC) was found to be 215 meq/100 g zeolite. Silver ions (Ag⁺) were loaded on the zeolite by placing it in contact with 0,1 M AgNO₃ solution at solid to liquid ratio = 1 : 20 for 6 hours, pH = 6 and magnetic stirring. Silver-loaded zeolite was washed with distilled water until negative reaction for Ag⁺ in washings was reached. The amount of Ag⁺ uploaded on zeolite (in this case 79 mg Ag/g zeolite) was calculated by using the data on the solution concentration before and after its contact with zeolite. More information on the zeolite modification and on the characterization of the metal-loaded zeolite can be found in our previous work [31, 32].

Stock solutions containing 1000 mg/L of Cr(VI) were prepared by dissolving K₂CrO₄ in distilled water. This solution was diluted with distilled water as required to obtain the solutions with different concentrations of Cr(VI) thus modelling polluted water. 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 by ICP-AES analysis after separating the solid and liquid phases by centrifugation (800 rev/min).

Experiments were conducted batch-wise: 0,5 g of zeolite, contacting with 50 mL of Cr(VI) bearing solution, was stirred with magnetic stirrer for corresponding time. Our preliminary studies showed as optimum the ratio 100 mL of wastewater to 1 g of zeolite (volume to mass – v: m) and the zeolite particles' size of 0,09-0,325 mm. Solutions containing Cr(VI) in the range from 5 to 30 mg/L (at pH 6) were deployed in the experiments aimed at studying the process kinetics, the impact of initial concentration of the pollutant and determining the adsorption isotherm. The impact of solutions pH value on the Cr(VI) immobilization was studied under the following conditions: concentration - 10 and 20 mg/L Cr(VI); contact time – 30 min and pH value of solutions to be treated 4, 6 and 8.

Table 1. Some parameters of the studied wastewaters

Water sample, Parameter	Sample 1	Sample 2	Sample 3
Ca ²⁺ , mg/L	11,6	2,0	73,1
Mg ²⁺ , mg/L	3,6	2,4	8,2
Na ⁺ , mg/L	90,3	49,9	26,2
K ⁺ , mg/L	0,7	1,9	3,3
HCO ₃ ⁻ , mg/L	125,9	97,1	237,1
CO ₃ ²⁻ , mg/L	6,0	18,0	-
SO ₄ ²⁻ , mg/L	109,1	70,4	66
Cl ⁻ , mg/L	12,4	7,8	7,2
Cr (VI), mg/L	16,8	23,2	33,8
Cu, mg/L	8,3	7,4	31,2
Zn, mg/L	19,3	8,8	61,2
pH	8,3	8,5	7,2
Cond., μS/cm	442	297	557

Desorption experiments were made in order to check how strongly Cr ions were immobilized by the silver modified zeolite. One g of preloaded zeolite (by its equilibration with solutions containing 20 mg/L Cr(VI))

was placed in contact for 8 h with 100 mL of distilled water and then the water was analyzed. The separated zeolite was dried and reused under the following conditions: 20 mg/L Cr(VI), pH 6, v: m = 100, 30 min.

In other series of experiments Ag⁺-loaded zeolite was placed in contact for 30 min at v: m = 100 with samples of industrial wastewater that was partially treated in an enterprise - Table 1.

Data obtained were processed with the aid of EXCEL program.

3 Equations used

The pollutant removal from the initial solution, was calculated using the equation (1):

$$Removal, \% = [(C_o - C_t) / C_o] \times 100 \quad (1)$$

where C_o is the initial and C_t is the pollutant concentration (mg/L) at time t (min).

The quantity of immobilized pollutant q_t (mg/g) was calculated according to equation (2):

$$q_t = (C_o - C_t) \times V / m \quad (2)$$

where C_o and C_t - as mentioned above, m is the mass of the adsorbent (g) and V is the volume of the solution, contacting with the adsorbent (L). When equilibrium is reached the relation gives the amount q_e, (mg/g) of pollutant immobilized per unit mass of the adsorbent at equilibrium:

$$q_e = (C_o - C_e) \times V / m \quad (2')$$

and C_e is the pollutant concentration at equilibrium (mg/L).

Experimental data have been fitted to the equations describing the pseudo first order (PFO) - (3), the pseudo second order (PSO) - (4) and the Elovich - (5) kinetic models [34]:

$$\ln (q_e - q_t) = \ln q_e - k_1 \times t \quad (3)$$

$$t / q_t = 1 / (k_2 \times q_e^2) + t / q_e \quad (4)$$

$$q_t = (1/\beta) \times \ln (\alpha \times \beta) + (1/\beta) \times \ln t \quad (5)$$

where t, q_e and q_t are as described above, k₁ is the PFO rate constant [time⁻¹, 1/min] and k₂ is the PSO rate constant of adsorption [concentration⁻¹ x time⁻¹, g/(mg x min)], α - the Elovich initial adsorption rate [concentration x time⁻¹, mg / (g x min)], β [concentration⁻¹, g/mg] - Elovich desorption constant.

Only data from the initial 20 min (that are not very close to the equilibrium) were considered, in order to avoid incorrect conclusions [35].

Isotherms equations that are most often tested in the literature for describing the adsorption from liquid phase, namely, Freundlich (6) and Langmuir (7) isotherms (used in their linear form) [17, 36], were checked for their ability to describe the adsorption equilibrium:

$$\log q_e = \log K_F + 1/n \times \log C_e \quad (6)$$

$$C_e / q_e = 1 / (K_L \times q_{max}) + C_e / q_{max} \quad (7)$$

where q_e , and C_e - as described above, K_F - Freundlich constant $[(\text{mg/g})/(\text{L/mg})^{1/n}]$, K_L is the Langmuir equilibrium constant (L/mg) - related to the free energy of adsorption and the reciprocal of the concentration at which half saturation of the adsorbent is reached, q_{max} (mg/g) is the maximum adsorption capacity, calculated by using equation (7).

Temkin isotherm (8) that takes into the account the adsorbent-adsorbate interactions and the Redlich-Peterson isotherm (9) featuring both Langmuir and Freundlich isotherms and describing sorption on heterogeneous surfaces were also checked (in their linear form) [17, 36] for their ability to describe the process:

$$q_e = B \ln A + B \ln C_e \quad (8)$$

$$\ln(C_e/q_e) = \beta \times \ln C_e - \ln k_R \quad (9)$$

where A [L/mg] - equilibrium binding constant that relates to the maximum binding energy, $B = R \times T / b$ is related to the heat of adsorption, R - gas constants $([\text{J}/(\text{mol}\times\text{K})])$, T - temperature [K], b - the Temkin isotherm constant [J/mol], k_R - the Redlich-Peterson constant [L/mg] and β - dimensionless heterogeneity factor, q_e , and C_e - as described above.

4 Results and discussion

Results for Cr(VI) removal from model water as function of time at different initial pollutant concentrations are presented in Figure 1.

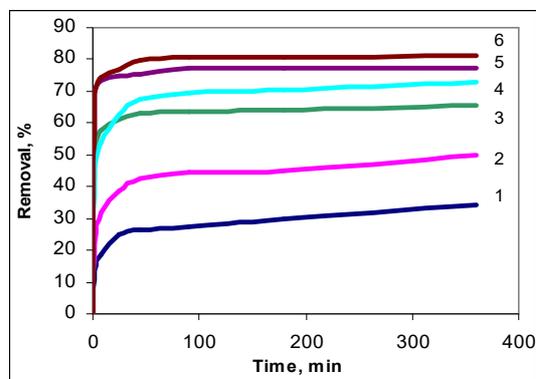


Fig. 1. Removal of Cr(VI) as function of time at different initial concentrations: 1 - 5 mg Cr(VI)/L, 2 - 10 mg Cr(VI)/L, 3 - 15 mg Cr(VI)/L, 4 - 20 mg Cr(VI)/L, 5 - 25 mg Cr(VI)/L, 6 - 30 mg Cr(VI)/L, pH 6, $v : m = 100$

As it can be seen from the Figure 1, the major part of the Cr(VI) removal occurred in the initial 25-30 min. That is why contact time of 30 min has been chosen in experiments aimed at studying the possible differences in Cr(VI) removal, due to influence of initial pH value of solution as well as the Cr(VI) removal from the real wastewater.

The immobilized amounts of Cr(VI) are of the same order of magnitude as the values described by other works for metal-exchanged (with best results for lead ions) forms of different aluminosilicate minerals, including natural clinoptilolite [25, 27]. However, use of Ag^+ -loaded zeolite is more environmentally friendly,

compared to Pb-loaded, and the additional advantage is the antibacterial activity of the material.

As it can be seen in the Figure 1, increasing the initial concentration of Cr(VI) increases both the removal (%) and the absolute removed amount of pollutant (mg/g). Similar influence of the initial pollutants concentration was found for the Cr (VI) removal by Martínez and co-authors [37].

The experimental data fitting to equations (3) - (5) showed that Cr(VI) ions immobilization is best described by the PSO kinetic equation, for which the coefficients of determination (R-squared) were the highest, followed by the Elovich model - Table 2. Similar order of kinetics models suitability is found for describing the adsorption of other noxious (arsenic) anions from aqueous solutions by use of manganese ferrite nanoparticles [34].

Table 2. The R^2 value for the studied kinetic models of Cr(VI) removal from model wastewater

Initial concentration, mg/L; Models	Pseudo-first order	Pseudo-second order	Elovich
5	0,993	0,994	0,982
10	0,945	0,999	0,996
15	0,960	0,999	0,997
20	0,986	0,999	0,994
25	0,989	0,999	0,998
30	0,992	0,999	0,995

Generally, kinetics description by the pseudo-second-order equation indicates that the rate-limiting step of immobilization process is of chemical nature. The removal process depends on the concentration of the dissolved pollutant in the solution and the available fraction of active sites of the adsorbent [38]. Most probably, the explanation lies in the formation of low soluble Ag_2CrO_4 on the adsorbents surface.

Another way to check the model adequacy is to compare experimental and calculated with the model values for the quantity of immobilized pollutant - Table 3 (data at 25th min). As it can be seen from Table 3, the PSO kinetic model quite satisfactory describes the process, the relative error for the calculated adsorbed amount is less than 10 % at all initial concentrations of Cr(VI).

The Elovich equation is generally applied to describe satisfactory kinetics of chemisorption for systems with heterogeneous adsorbing surfaces [34]. The relatively high values of R^2 obtained also for the Elovich equation implies the surface heterogeneity of the used modified clinoptilolite.

Table 3. Comparison of q_{exp} and q_{model} , calculated with PSO model.

Initial concentration, mg/L	q_{exp} , mg/g	q_{model} , mg/g
5	0,187	0,206
10	0,396	0,427
15	0,939	0,956
20	1,257	1,311
25	1,846	1,862
30	2,286	2,380

Experimental data fitting to the isotherm equations (6) - (9) showed that the process is well described by the Freundlich isotherm - Table 4.

Table 4. The R² value for the studied isotherm models of Cr(VI) removal from model wastewater.

Model	Freundlich	Langmuir	Temkin	Redlich–Peterson
R ²	0,995	0,897	0,937	0,985

In addition, the amounts q_e (mg/g) of pollutant immobilized per unit mass of the adsorbent at equilibrium, calculated using that model are near to the experimentally found (the relative error for the calculated adsorbed amount is less than 10 % for all studied initial concentrations) - Table 5. The process description by the Freundlich isotherm indicates that sorption occurs on heterogeneous surfaces, and the obtained value n < 1 implies on the chemical nature of the bonding [17, 36].

Table 5. Comparison of q_{exp} and q_{e,calc.}, calculated with Freundlich model.

Initial concentration, mg/L	q _{e,exp} , mg/g	q _{e,calc.} , mg/g
5	0,256	0,2605
10	0,508	0,5329
15	1,0005	0,9106
20	1,461	1,3835
25	1,908	1,9929
30	2,415	2,5004

The immobilization process description by the PSO and Freundlich models has been reported also by other authors for Cr(VI) removal from waters by surfactant modified zeolite [19, 21].

Results showing the impact of wastewater initial pH value on Cr(VI) removal efficiency are presented in Table 6. As it can be seen from Table 6, the Cr(VI) removal is increased at higher pH value. Similar trend was observed for clinoptilolite modified with barium and zinc [27]. The findings could be attributed to the presence of different species of Cr(VI) at different pH values, and their affinity to silver and the stability of the formed surface species [17].

Results from desorption experiments showed that about 2 % of Cr(VI) were immobilised.

Table 6. Influence of wastewater initial pH on the Cr(VI) removal, in %, for 30 min

Initial Cr(VI) concentration / pH	4	6	8
10 mg/L	2,4	40,4	43,0
20 mg/L	3,6	65,6	82,4

When the zeolite was reused, the Cr(VI) removal in 30 min was 43,8 % implying for the possible use of the zeolite in more than one cycle.

Results from experiments with industrial wastewaters are presented in Table 7.

Considering the complicated water matrices (compared to the model water - i.e. solutions prepared with distilled water), surprisingly good results for the

Cr(VI) removal were found. Having in mind the parameters of the studied water samples (Table 1), as well as the observed influence of the initial pollutant concentration and the initial pH value (found for model waters - Figure 1 and Table 6), the good results could be ascribed to the impact of those factors.

Table 7. Pollutants removal from wastewater, in %, for 30 min

Water, pollutant	Sample 1	Sample 2	Sample 3
Cr(VI)	80,54	95,98	91,03
Cu(II)	95,1	86,6	76,7
Zn(II)	78,3	71,4	69,8

An additional positive result is the immobilization of copper and zinc ions, which is not unexpected and could be related to the unused entirely sorption capacity of the zeolite at its loading with silver ions.

5 Conclusions

Modification of natural Bulgarian zeolite - clinoptilolite by its loading with silver ions renders it able to immobilize Cr(VI) from practically neutral to slightly alkaline industrial wastewater.

Increasing the initial pollutant concentrations in the model wastewater (in the studied range) increases the removed amount (reaching 80 % in 45 min at initial concentration of Cr(VI) = 30 mg/ L).

The kinetics of Cr(VI) immobilization by the Ag-modified zeolite is best described by the pseudo-second order kinetic equation that is indicative for the chemical nature of the rate-limiting step of the Cr(VI) immobilization.

The data obtained are best fitted to the Freundlich adsorption isotherm.

The silver-loaded clinoptilolite removes in 30 min over 80 % of Cr(VI), over 75 % of Cu(II) and over 70 % of Zn(II) that present simultaneously in industrial wastewater.

In conclusion, we can say that due to its ability to remove Cr(VI) species in combination with some heavy metal ions and some organic pollutants, as well as the exhibited antibacterial activity, silver loaded clinoptilolite deserves further investigation as a multifunctional reagent in the wastewaters treatment.

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