Textile wastewater treatment using green sorbent

Obrada otpadnih voda tekstilne industrije korištenjem zelenog adsorbensa

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Abstract

Wastewater from the textile industry contains large quantities of heavy metal ions such as Cr(VI), Zn(II), Pb(II) and Cd(II). They are often used for the production of color pigments for textile dyes. The free discharge of such waste water into the environment would cause major environmental problems. The presence of toxic Cr(VI) in the aquatic environment has been shown to be one of the major environmental problems. This article reports on the technical applicability of a low-cost green sorbent, nanoporous bentonite, as an adsorbent for the elimination of Cr(VI) ions from textile wastewater. The batch adsorption experiment was carried out to determine the influence of different working parameters (initial metal ion concentration, pH, amount of adsorbent) on the removal efficiency of Cr(VI). The experimental data were interpreted using the first and second order pseudokinetic model.

Keywords: textile wastewater; Cr(VI) ions; adsorption; green adsorbent; nanoporous bentonite

Sažetak

Otpadne vode tekstilne industrije sadrže velike količine iona teških metala, kao što su Cr(VI), Zn(II), Pb(II) i Cd(II), a koji imaju veliku primjenu u proizvodnji bojila za tekstil. Ispuštanje takvih nepročišćenih otpadnih voda može izazvati velike probleme u okolišu. Prisutnost toksičnog Cr(VI) u vodenom okolišu jedan je od najozbiljnijih ekoloških problema. U ovom radu prikazana je tehnička primjenjivost zelenog adsorbensa niske cijene, nanoporoznog bentonita, za uklanjanje Cr(VI) iona iz otpadnih voda tekstilne industrije. Postupak adsorpcije proveden je batch postupkom sa ciljem utvrđivanja utjecaja nekoliko radnih parametara (početna koncentracija metalnog iona, pH vrijednost, količina adsorbensa) na učinkovitost uklanjanja Cr(VI). Eksperimentalni podaci interpretirani su pomoću pseudokinetičkog modela prvog i drugog reda.

Ključne riječi: otpadne vode tekstilne industrije; Cr(VI); adsorpcija; zeleni adsorbens; nanoporozni bentonit

1. Introduction

Population growth requires both, the development and expansion of the textile industry. At the same time, the textile industry, which uses a large number of different types of chemicals and dyes, is considered the biggest polluter of the environment [1]. At various stages of textile manufacturing, different contaminants are being released to the environment. Chromium is the most abundant heavy metal in color pigments and textile dyes and therefore the wastewaters from the textile industry contain a large amount of Cr(VI) from 10 to 3000 mg/l [2]. In terms of human health, the most harmful form of chromium is its hexavalent cation because it is carcinogenic. The concentrations of Cr(VI) ions in the textile wastewaters are high and exceeds the maximum allowed value in effluents which is 0.05 mg/l. In order to achieve the values required by the environmental regulations, the amount of Cr(VI) in the output streams must be reduced [3]. Therefore, many researchers are investigating the possibilities of reducing the concentration of Cr(VI) ions from water systems, applying various techniques, like adsorption, membrane processes, electrolysis, chemical precipitation, ion-exchange, coagulation [4-13]. Adsorption of Cr(VI) is widely applied method for heavy metal elimination due to its simplicity of operation, efficiency and financial viability [6,14]. Different materials are studied as possible adsorbents for heavy metals elimination from aqueous solutions, such as zeolites, silicates, red mud, floating ashes, certain types of natural or agricultural waste [15-20]. Generally, natural or agricultural wastes contain various functional groups such as hydroxyl, aldehyde, aliphatic acid group, alkene, amide, nitro-aromatic, silicate, sulfonate and others. The existence of those functional groups in bio-adsorbents, facilitates adsorption of Cr(VI). Rice husk and potato peel, bark Eucalyptus, water hyacinth roots and many more low cost biosorbents have been investigated for adsorption of hexavalent chromium from wastewater [21-23].

The use of bentonite as a material suitable for the adsorption of heavy metals from aqueous solutions is very common [24-26]. The adsorption properties of bentonite, originated from Macedonia, for reduction of Cr(VI) ions from wastewaters have been analysed and are presented in this article.

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2. Experimental part

2.1. Materials and methods

Adsorbent

The removal of Cr(VI) ions from water solutions was performed by adsorption using nano-bentonite as green adsorbent. The applied bentonite in this work is local material originated from Ginovce, Macedonia, previously characterized [26]. Bentonite was converted into nano form by grinding in an attritor mill and particles with dimensions of about 70 nm were obtained, determined by SEM microscopy.

Chemicals

In this adsorption experiment were used: standard solution of $K_2Cr_2O_7$ (1 g/l), 0.1 M HCl, and 0.1 M NaOH (used for pH adjustment) and they were all analytical grade.

Adsorption experiment

Batch adsorption experiment (laboratory glass reactor of 2l, magnetic stirring at 400 rpm, room temperature, 3h) was performed to obtain the data for Cr(VI) removal efficiency of nano-bentonite. The influence of pH (1, 2 and 3), bentonite amount (0.5, 1.5, 2.5, 3.5, 4.5 and 5.5 g/l) and the effect of initial metal ions concentration (0.3, 0.4, 0.5 and 0.7 mg/l) were investigated. UV/Vis type Prove 600 was used to determine the Cr(VI) concentrations in standard and treated solutions after adsorption experiments by ASTMD6832 standard test method for the determination of hexavalent chromium using 1,5-diphenylcarbazide.

3. Results and discussion

The efficiency of the adsorption of metal ions is expressed by the removal percentage, which is determined by the equation:

$$\%R = \frac{C_0 - C_e}{C_0} \cdot 100 \qquad (1)$$

where C_0 [mg/l] is initial concentration of the Cr(VI) ions and C_e [mg/l] is equilibrium concentration of Cr(VI) ions.
The equation 2 is used for calculation of the adsorbed amount of metal ion, qt [mg/g]:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \qquad (2)$$

where C_t [mg/l] is concentration of Cr(VI) at time t, V is the volume of the solution [l] and m is the mass of the adsorbent [g].
Pseudo first and pseudo second - order kinetic models were used to process experimental data. Their linear forms are expressed with the equations 3 and 4, respectively:

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

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (4)$$

where q_e [mg/g] is the adsorbed amount of metal ion at equilibrium, k_1 [1/min] is the pseudo first-order rate constant, k_2 [g/mg·min] is the rate constant for pseudo second-order adsorption.

Influence of pH

The pH value of the solution is a very important parameter that strongly affects the adsorption efficiency. The influence of the pH values of 1, 2 and 3 on the removal of Cr(VI) ions by nanobentonite, was analyzed in this study and the results are shown in Figure 1.

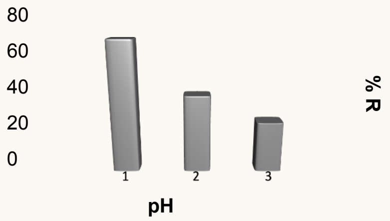

Figure 1. Influence of pH on Cr(VI) adsorption on nano-bentonite (room temperature, V = 2l, C_0 = 0.5 mg/l, nano-bentonite dose = 2.5 g/l, 400 rpm)

The obtained results show that at pH 1, the highest value of the removal percentage of Cr(VI) is determined, R_{max} = 71 %. This occurs because the surface of the used material – nano-bentonite, was activated with surface protonation by addinng the acid. $HCrO_4^-$ is the form at which chromium ions exist when the pH value of the solution is low.

Influence of the adsorbent dose

The influence of the nano-bentonite dose of 0.5; 1.5; 2.5; 3.5; 4.5 and 5.5 g/l on the efficiency of elimination of Cr(VI), was also investigated in this study and the results are given in Figure 2.

It can be seen that increasing the dose of the adsorbent from 0.5 to 2.5 g/l leads to an increase in the removal percentage of Cr(VI) ions from 38 to 68 %, respectively, and this is due to the availability of more active sites on larger contact area. At an adsorbent amount higher than 2.5 g/l, the adsorbent particles agglomerate and thus reduces the active surface area, resulting in lower efficiency of removal of metal ions.

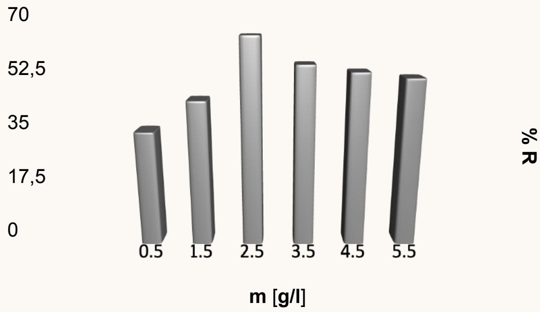

Figure 2. Influence of amount of nano-bentonite on Cr(VI) adsorption (room temperature, V = 2l, C_0 = 0.5 mg/l, pH = 1, 400 rpm)

Influence of the initial metal ion concentration

The impact of the initial concentration of metal ions (0.3, 0.4, 0.5 and 0.7 mg/l) on the removal efficiency of Cr(VI) by nano-bentonite is shown in Figure 3.

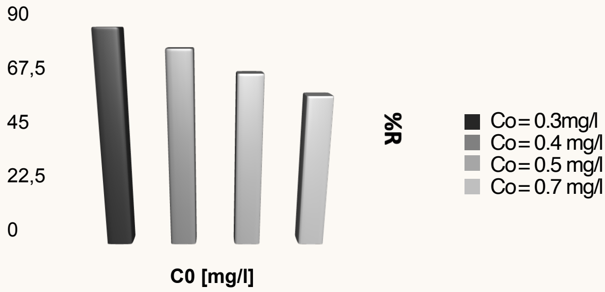

Figure 3. Influence of initial Cr(VI) concentration on adsorption efficiency on nano-bentonite (room temperature, V = 2l, pH = 1, nano-bentonite dose = 2.5 g/l, 400 rpm)

The lowest value of the Cr(VI) concentration of 0.3 mg/l show the greatest degree of reduction of the examined metal ions of 87%. After that, increasing the initial concentration at 0.4, 0.5 and 0.7 mg/l, leads to a decrease of the removal percentage to 80%, 71% and 62%, respectively. Such dependence occurs because at low values of the concentration of metal ions, on the surface of the bentonite there are enough active centers on which the ions of the adsorbate are adsorbed, but when the initial concentrations are higher, saturation of the adsorption centers occurs, leading more Cr(VI) to remain in the solution.

Kinetic studies

The interpretation of the experimental data have been done using the pseudo first and the pseudo second-order kinetic models. The results of the kinetic investigation are shown in Figures 4 and 5.

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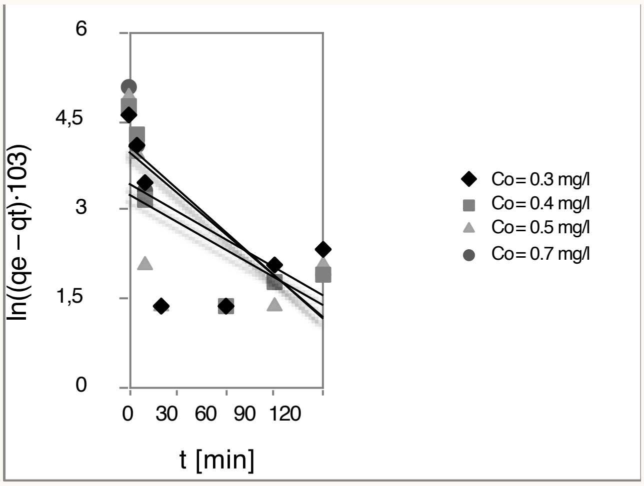

Figure 4. Pseudo first-order model for Cr(VI) adsorption on nano-bentonite

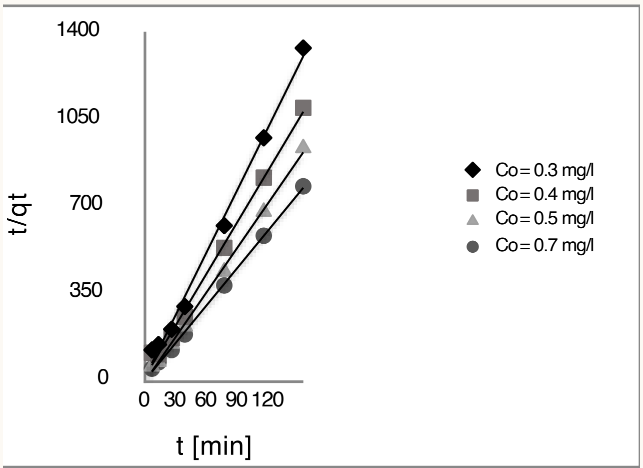

Figure 5. Pseudo second-order model for Cr(VI) adsorption on nano-bentonite

The kinetic parameters for analyzed kinetic models and the correlation coefficients, R^2, for Cr(VI) adsorption on the nano-bentonite, are presented in Table 1. The better linearity of the plots on Figure 5 as well as the higher values of the correlation coefficients, reveal that the adsorption of Cr(VI) ions on nano-bentonite follows pseudo second-order kinetics and that chemisorption is the rate-limiting step. The pseudo first-order model can not be used to describe the kinetics of the analyzed adsorption system.

Table 1. Kinetic parameters for Cr(VI) adsorption on nano-bentonite

Kinetic model	Parameters	Cr(VI) ions			
	$C_{0,exp.}$ [mg/l]	0.3	0.4	0.5	0.7
	$q_{e,exp.}$ [mg/g]	0.100	0.116	0.136	0.160
Pseudo first-order	k_1 [1/min] q_e [mg/g] R^2	0.0157 0.0315 0.3254	0.0232 0.0538 0.6899	0.0155 0.0262 0.2953	0.0242 0.0594 0.6889
Pseudo second-order	k_2 [g/mg·min] q_e [mg/g] R^2	6.3234 0.0932 0.994	4.0106 0.1128 0.9953	116.37 0.1305 0.9981	8.3891 0.1554 0.999

4. Conclusions

The results of this study indicate the importance of operating parameters, such as pH, adsorbent amount and initial metal ion concentration, on the efficiency of removal of metal ions from wastewater. The best removal percentage was obtained at pH of solution 1, using 2.5 g/l of the applied nano-benotnite and at the lowest initial concentration of Cr (VI), in this case 0.3 mg/l. Pseudo second-order kinetic model can be applied to describe the adsorption kinetics of Cr(VI) onto nano-bentonite. The obtained results of this adsorption experiment, give us the right to conclude that for efficient treatment of industrial wastewaters, in terms of Cr(VI) reduction, the analyzed bentonite with Macedonian origin, converted into nano form with grinding in an attritor mill and activated by surface protonation, can be effectively applied as low-cost green adsorbent.

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