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KINETIC STUDY FOR THE REMOVAL OF Cr(VI) IONS FROM AQUEOUS SOLUTIONS BY NATURAL PEMZA

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Abstract

A large part of industries discharge wastewater containing toxic substances without any prior treatment. Pollution of the environment, especially with water containing heavy metals, is a very serious problem today. Among these heavy metals, chromium is one of the most dangerous. In this paper, for the removal of Cr(VI) from aqueous solutions, we used pemza, raw inorganic material from Bojanciste, near Kavadarci, Republic of North Macedonia. With special emphasis, we have focused on studing the kinetics of the adsorption process of chromium ions with low-cost adsorbent, pemza. From the results of this research we have concluded that the correlation coefficients are higher (R^2>0.99) for pseudo second–order reactions. At the same time, the experimental values q_e agree with the values calculated by applying this kinetic model. This indicates that the kinetic reaction for the Cr(VI)-pemza system proceeds according to this mechanism.

Keywords: adsorption, kinetics, natural pemza, Cr(VI) ions.

1. INTRODUCTION

Industrial wastewater, sewage and waste are the main factors for the contamination of the soil and the living environment as a whole [1]. The majority of pollutants are heavy metals from wastewater from the metal processing, leather, pharmaceutical, pesticide, organic chemical, rubber, plastic, wood products industries [2]. Heavy metals are released into the watercourses and contaminate water sources near the industrial sites. To avoid health risks, it is essential to remove these toxic heavy metals from wastewater before they are discharged [3]. Most of the heavy metals released into wastewater are toxic and carcinogenic and pose a high risk to human health [4, 5].

The release of large quantities of hazardous materials into the environment results in a large number of ecological problems and due to their non-degradability, they can accumulate in the food chain and thus pose a high risk to human health [6]. One of the most dangerous metals is chromium. Our goal was to remove Cr(VI) from aqueous solutions using an adsorption process with cheap adsorbent [7].

There are several methods for treating wastewater containing chromium: ion exchange, membrane separation, neutralization method, reduction, biological method and adsorption method [8]. The adsorption method has unique advantages due to the selectivity of the adsorbent material, low cost, regeneration of the adsorbent and not only solves the problem of expensive chemical methods but also overcomes the shortcoming of the limited adsorption capacity of the biological process [9, 10].

Total chromium can be detected by atomic absorption spectroscopy (AAS) and other instrumental methods. Cr(III) and Cr(VI) can be detected by ion chromatography. Cr(VI) can also be detected by titration with a standard mixture of $Na_2S_2O_4$ and I_2 [11].

2. MATERIALS AND METHODS

The pemza sample was prepared mechanically in a ball mill with granulation where the fraction of -0.5+0.25 mm dominates. For the preparation of working solutions, a standard solution of $K_2Cr_2O_7$ with a concentration of 1000 mg/l was used. Spectrophotometric analysis (UV/VIS Spectrophotometer Prove 600, Perkin Elmer, Norwalk, CT, USA) was used to determine the concentration of Cr(VI) ions before and after the adsorption process. For the spectrophotometric determination of chromium as Cr(VI) the 1,5-diphenylcarbazide method was used as validated in the standard methods for the investigation of drinking water and wastewater.

In order to define the kinetics of the Cr(VI) ion separation process, a series of experiments have been performed. The pemza that is the subject of the research was analyzed in a 2l laboratory reactor, at room temperature, with a constant stirring regime of 400 rpm with magnetic stirring, at pH 1 and 2 with an initial concentration of Cr(VI) ions 0.3, 0.4, 0.5 and 0.6 mg/l.

2.1. Kinetic studies

In order to define the adsorption kinetics of Cr(VI), the kinetic parameters for the adsorption process were studied for contact times from 1 to 240 minutes with monitoring of the removal process of Cr(VI) ions. The experimental values are shown with I order, II order, pseudo first-order, pseudo second-order and Elovic kinetic equations. The results show that the adsorption process follows the model of pseudo second-order.

3. RESULTS AND DISCUSSION

In this paper, the kinetics of the adsorption process of Cr(VI) ions with pemza has been studied by applying these kinetic models: first-order, second-order, pseudo first-order, pseudo second-order and Elovic model. The conformity between experimental values and model values is expressed through the correlation coefficient R^2. A higher value of R^2 for a kinetic model successfully describes kinetics of the Cr(VI) adsorption. The parameters of the applied kinetic model equations are obtained as values of the slope of the curve and the intercept from the obtained linear graphs. The parameters and correlation coefficients obtained from all kinetic models applied to the Cr(VI)-pemza system are presented in Tables 1 and 2.

By analyzing the values given in table, we can conclude that the correlation coefficients have higher values (R^2>0.99) for pseudo second-order reactions, foe all concentrations of Cr(VI) ions. At the same time, the experimental values q_e are in excellent agreement with the values calculated by applying this kinetic model. This means that the kinetic reaction for the investigated system proceed according to this mechanism. From here, chemisorption is the rate limiting step for the process, which involves valence forces through the separation and exchange of electrons between metal ions and functional groups of the adsorbent. The figure below shows a linear plot of the linear dependence of t/q_t versus t from the kinetic model for the pseudo second order reaction for the Cr(VI)-pemza system.

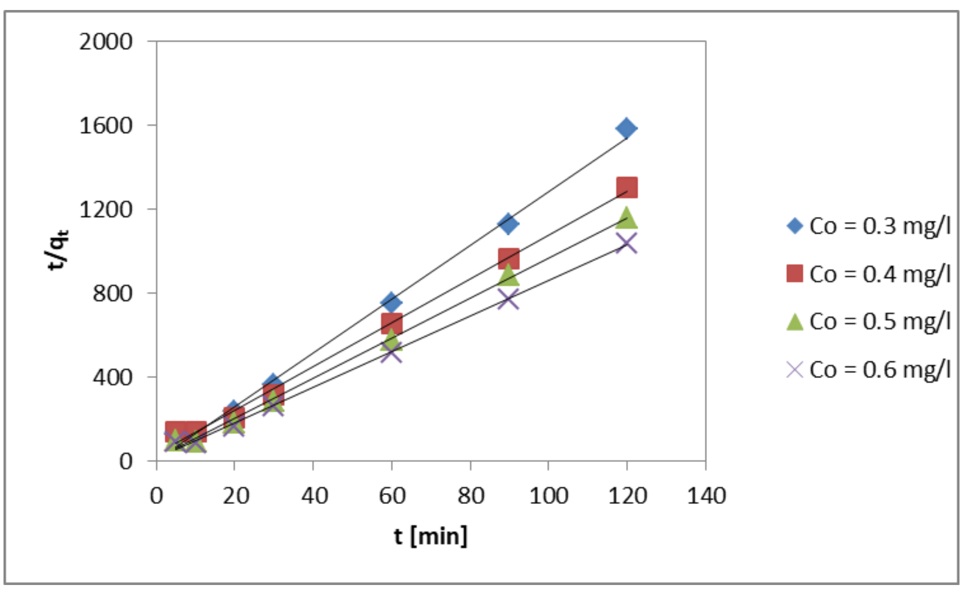

Figure 1. Pseudo second-order model for Cr(VI) adsorption on pemza, pH=1

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Table 1

Parameters for kinetic adsorption, Cr(VI)-pemza, pH=1

Kinetic model	Parameters	Metal ion Cr(VI)			
	C_0, exp. [mg/l]	0.3	0.4	0.5	0.6
	q_e, exp. [mg/g]	0.084	0.096	0.108	0.096
I-order reaction	k_1 [min^{-1}] C_0 [mg/l] R^2	0.0043 0.1464 0.1767	0.0048 0.2533 0.3654	0.0032 0.3148 0.2394	0.003 0.3978 0.26
II-order reaction	k_2 [l/mg·min] C_0 [mg/l] R^2	0.0241 0.1286 0.1277	0.0204 0.2374 0.3676	0.0097 0.2988 0.2278	0.0074 0.3816 0.2558
Pseudo I-order reaction	k_1 [min^{-1}] q_e [mg/g] R^2	0.0172 0.0228 0.2873	0.0275 0.0499 0.8082	0.0233 0.0362 0.528	0.0268 0.0421 0.6172
Pseudo II-order reaction	k_2 [g/mg·min] q_e [mg/g] R^2	410.6349 0.0779 0.9961	3.4827 0.0957 0.9956	7.9002 0.1049 0.9979	5.6437 0.1183 0.9979
Elovic	α [mg/g·min] β [mg/g] R^2	7.4755 136.9863 0.2901	0.1330 67.5676 0.6086	4.5347 97.0873 0.3535	2.6885 80.6452 0.3862

From Table 1, it can be seen that the coefficients of correlation R^2>0.99 have the high values in the pseudo second-order model, from here we can conclude that the kinetic adsorption of Cr(VI) with pemza, can be described by the model of pseudo second-order.

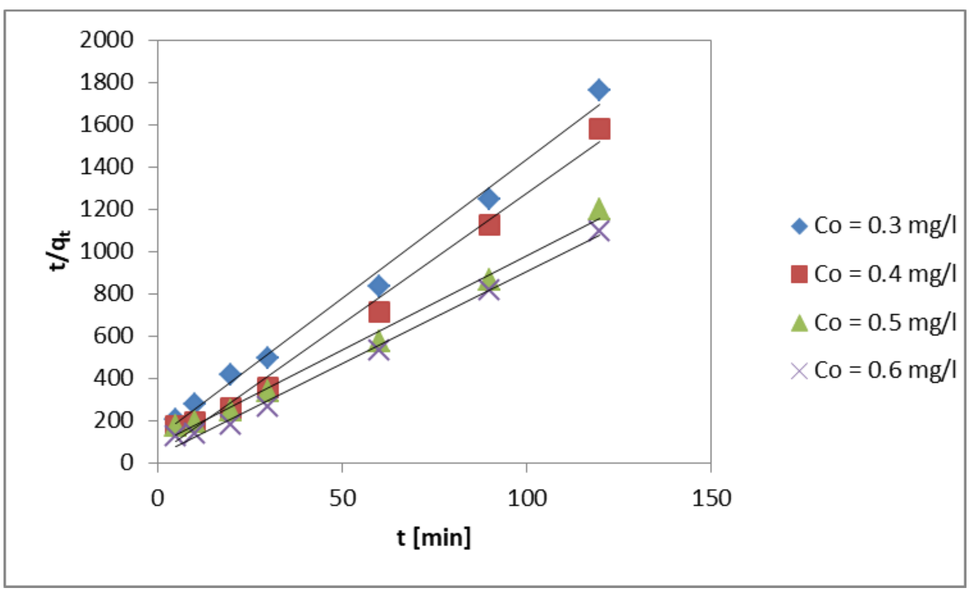

Figure 2. Pseudo second-order model for Cr(VI) adsorption on pemza, pH=2

Table 2

Parameters for kinetic adsorption Cr(VI)-pemza, pH=2

Kinetic model	Parameters	Metal ion Cr(VI)			
	C_0, exp. [mg/l]	0.3	0.4	0.5	0.6
	q_e, exp. [mg/g]	0.072	0.084	0.104	0.1132
I-order reaction	k_1 [min^{-1}] C_0 [mg/l] R^2	0.0061 0.2355 0.6829	0.004 0.2854 0.3991	0.005 0.4007 0.6454	0.0037 0.449 0.4303
II-order reaction	k_2 [l/mg·min] C_0 [mg/l] R^2	0.0334 0.2311 0.7222	0.0153 0.2745 0.3975	0.0151 0.3937 0.6905	0.0089 0.4324 0.4433
Pseudo I-order reaction	k_1 [min^{-1}] q_e [mg/g] R^2	0.0217 0.04464 0.8604	0.0186 0.0393 0.5972	0.0248 0.0628 0.8597	0.0279 0.0389 0.5539
Pseudo II-order reaction	k_2 [g/mg·min] q_e [mg/g] R^2	1.3655 0.0766 0.9922	3.6620 0.0813 0.9895	0.8775 0.1126 0.992	2.0357 0.1152 0.9945
Elovic	α [mg/g·min] β [mg/g] R^2	0.0172 64.1026 0.9301	0.0513 67.5676 0.6827	0.0309 46.2963 0.9183	0.0734 49.2611 0.7096

From Table 2, it can be seen that the coefficients of correlation $R^2>0.99$ have the high values in the pseudo second-order model, from here we can conclude that the kinetic adsorption of Cr(VI) with pemza, can be described by the model of pseudo second-order. From the results of the table it can be seen that the correlation coefficients obtained from the graphs of linear dependence t/q_t in relation to time from the kinetic model for the pseudo second-order have higher values, greater than 0.98 for all the concentrations investigated. Kinetic models for the adsorption of Cr(VI) by pemza, pH=1

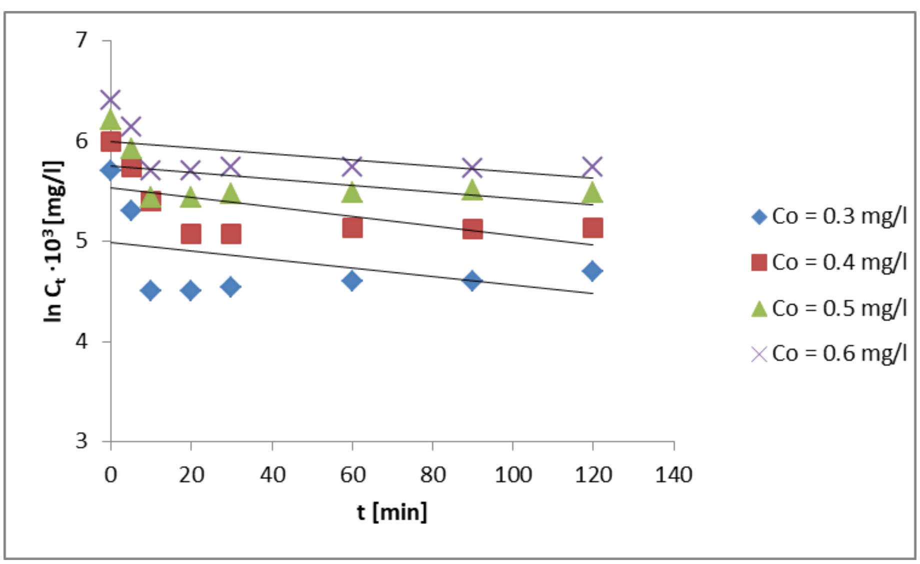

Figure 3. First-order model for Cr(VI) adsorption on pemza, pH=1

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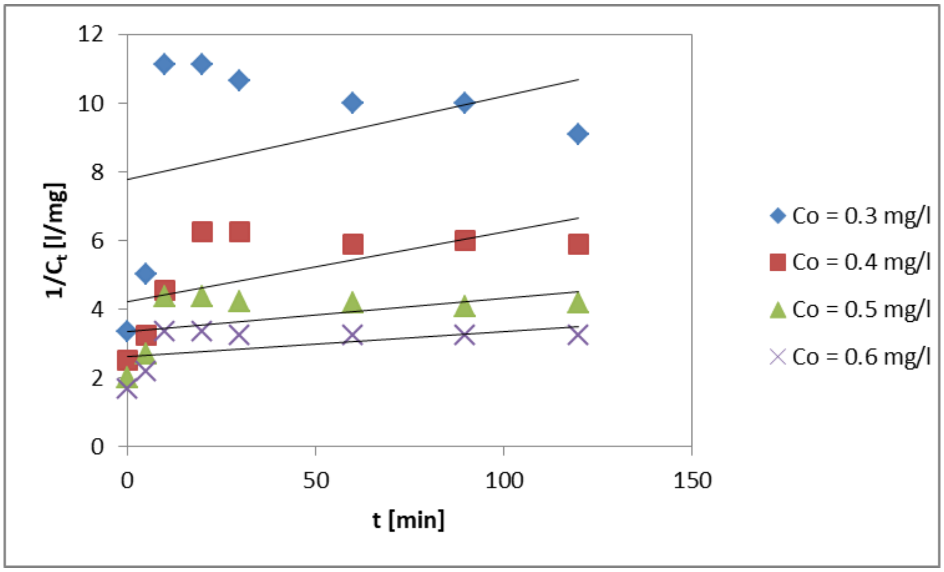

Figure 4. Second-order model for Cr(VI) adsorption on pemza, pH=1

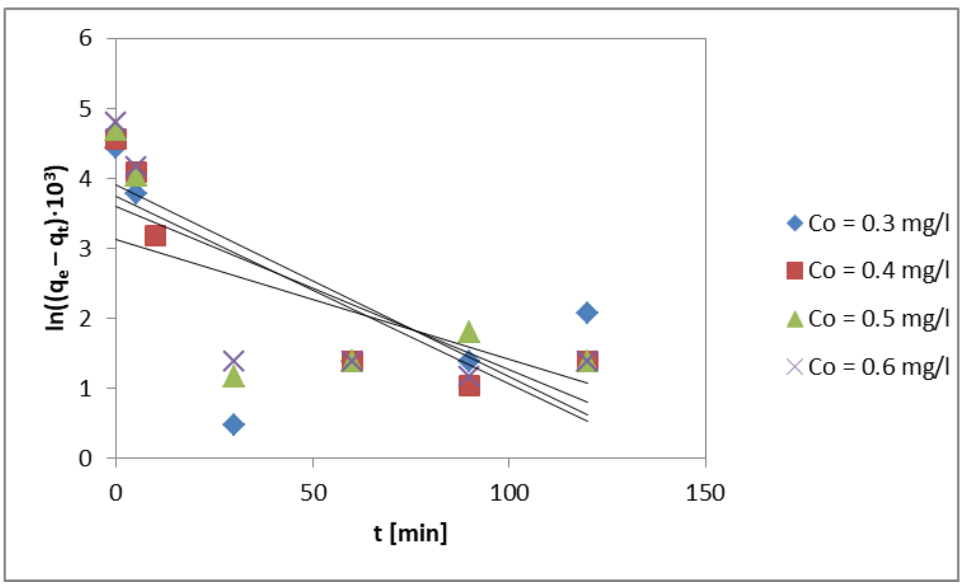

Figure 5. Pseudo first-order model for Cr(VI) adsorption on pemza, pH=1

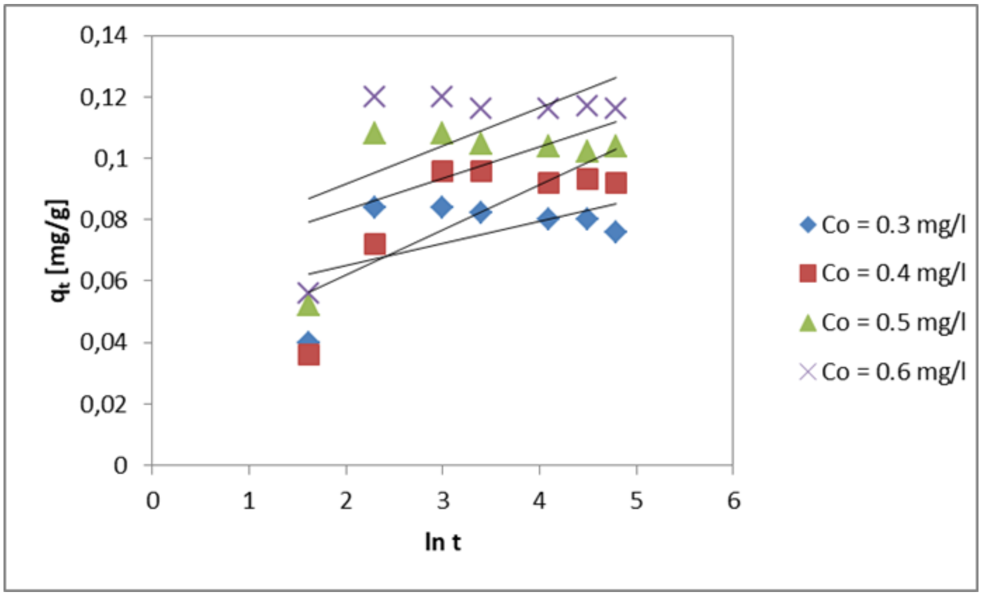

Figure 6. Elovic model for Cr(VI) adsorption on pemza, pH=1

Kinetic models for the adsorption of Cr(VI) by pemza, pH=2

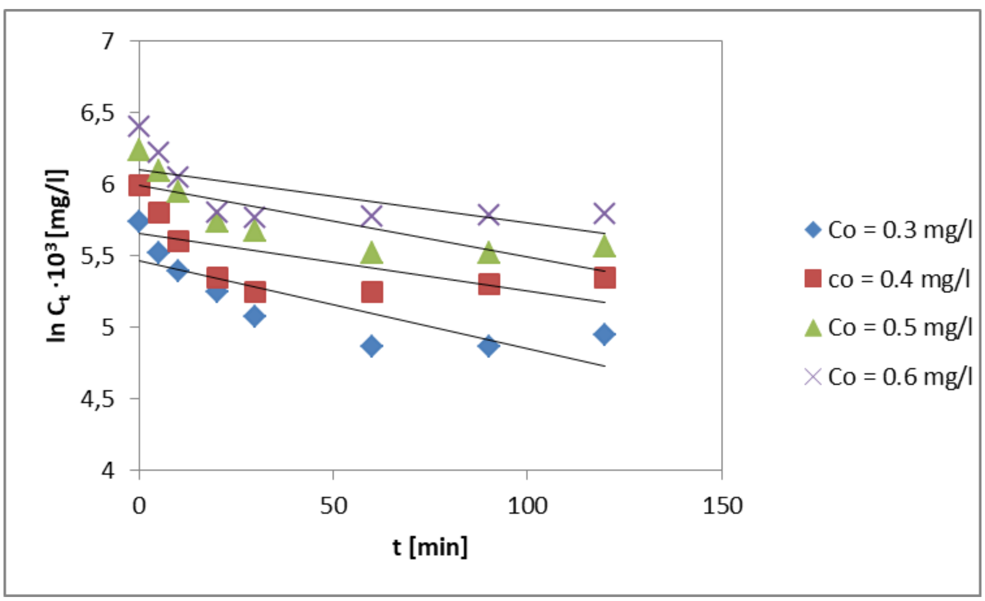

Figure 7. First-order model for Cr(VI) adsorption on pemza, pH=2

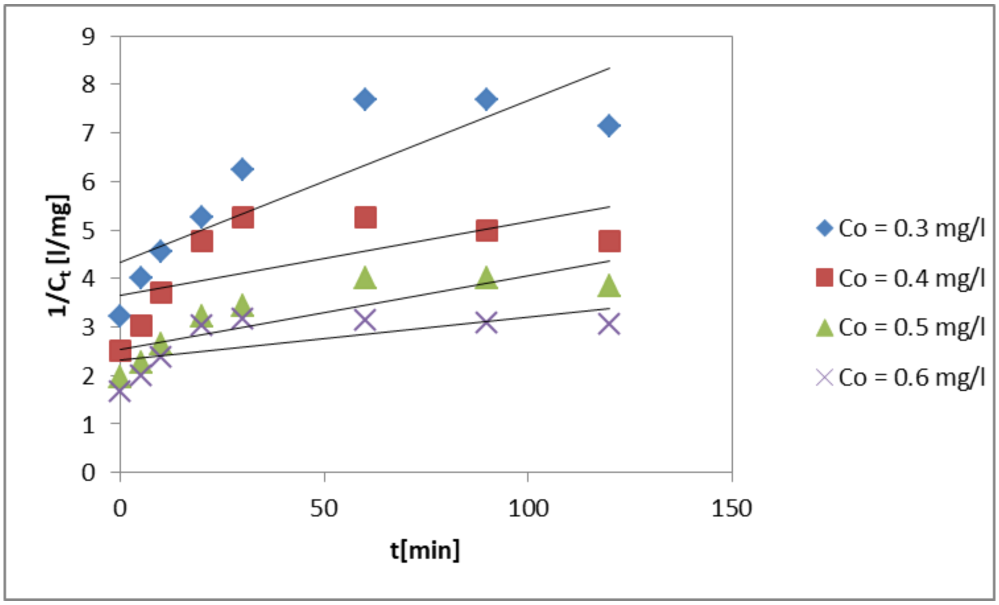

Figure 8. Second-order model for Cr(VI) adsorption on pemza, pH=2

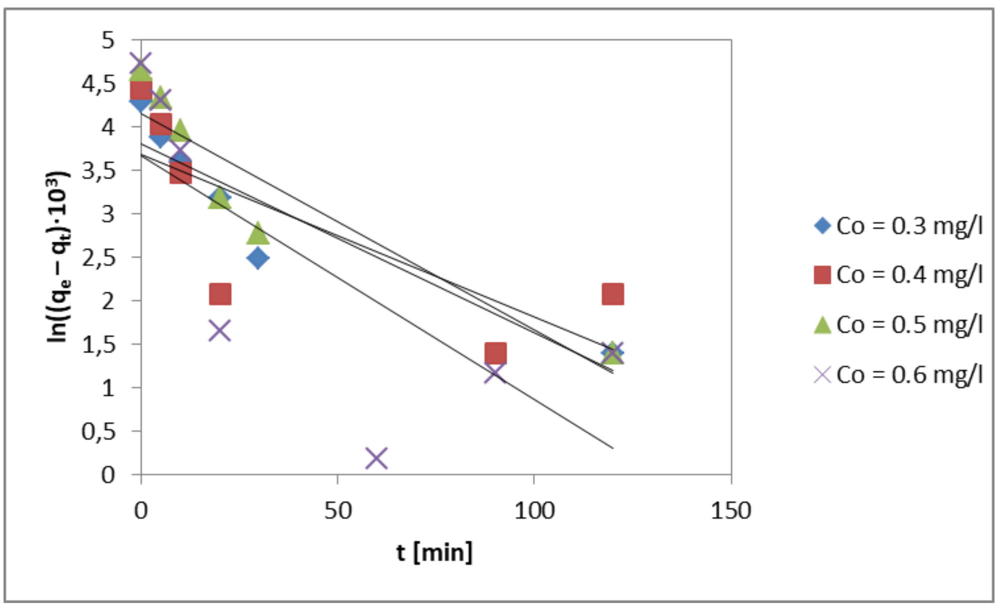

Figure 9. Pseudo first-order model for Cr(VI) adsorption on pemza, pH=2

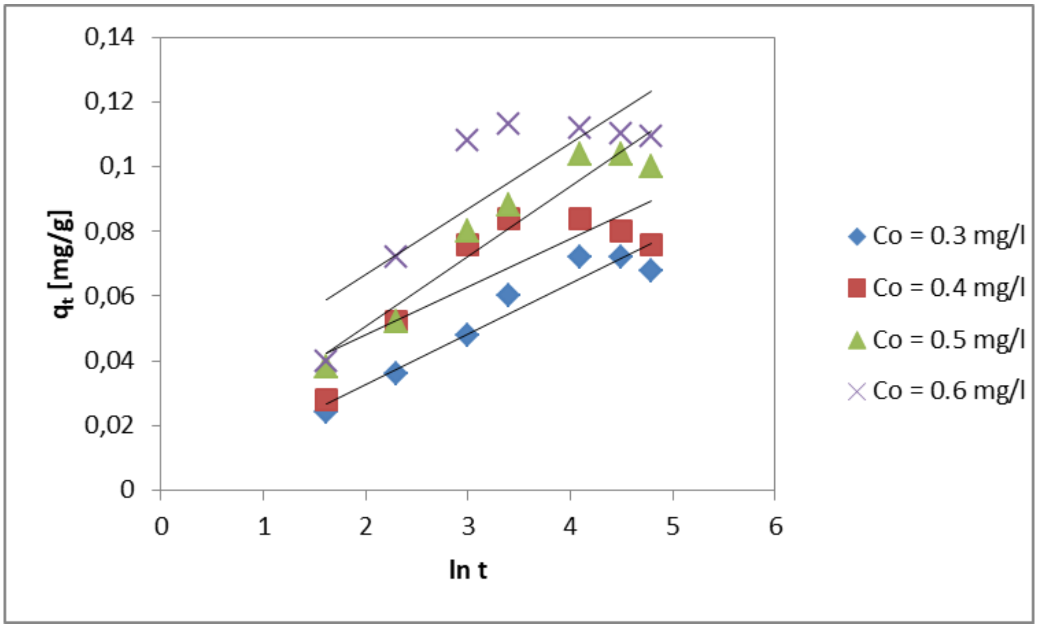

Figure 10. Elovic model for Cr(VI) adsorption on pemza, pH=2

4. CONCLUSIONS

In this paper, the removal of Cr(VI) ions with pemza (Bojanciste) was investigated. The pemza samples were used in their natural state without any treatment. The kinetics of Cr(VI) have been analyzed using these kinetic models: first-order, second-order, pseudo first-order, pseudo second-order, and Elovic model. From the kinetic parameters of adsorption it can be seen that the correlation coefficient R^2 has a higher value in the given pseudo second order model, and from here we can conclude that the kinetic adsorption of Cr(VI) by pemza can be best described by the pseudo second-order model. We can also conclude that natural pemza as a low-cost adsorbent can be used for the removal of Cr(VI) ions from aqueous solutions.

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