Professional paper

# SEPARATION OF Cr(VI) IONS FROM WATER RESOURCES BY GREEN INORGANIC SORBENT

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### Abstracta

Heavy metal pollution of water resources is a serious problem for the environment, especially with Cr(VI) ions, therefore, it is very important to efficiently remove them from polluted waters. The removal of Cr(VI) ions from water resources is very important due to their toxicity to living organisms and the environment. In this paper, we have selected natural mineral sorbent, clayey diatomite from Bitola, Republic of North Macedonia, for the elimination of Cr(VI) ions from real systems (groundwater and surface water). To determine the adsorption capacity, we used the spectrophotometric method (UV/VIS Spectrophotometer). The results we obtained from spectrophotometric analysis give us the initial concentration of Cr(VI) ions and the concentration of the ions after the adsorption process. To define the adsorption capacity of raw inorganic sorbent, clayey diatomite for the separation of Cr(VI) ions from real systems, we conducted research under these conditions: laboratory scale batch glass reactor with continuous stirring at 400 rpm, constant room temperature, with 0.5 mg/l initial Cr(VI) ions concentrations, adsorbent amount of 2.5 g/l, pH of the solution 2 and adsorption time from 1-120 min. From this research, we can conclude that inorganic natural mineral, clayey diatomite, can be used with high efficiency for the removal of Cr(VI) ions from real systems.

Keywords: Cr(VI), clayey diatomite, adsorption, real systems

#### 1. Introduction

Metals are present everywhere in the human environment. Some metals in certain amounts are important for vital functions, while some metals can be very dangerous to the human body. The presence of heavy metals in water resources can be of geogenic and anthropogenic origin. Industrial production contributes the most to the emission of heavy metals of anthropogenic origin. Many of these metals are toxic even at very low concentrations, which is why they have the potential to accumulate in the food chain. Heavy metals released into the aquatic environment bind to metals and ultimately accumulate in sediments [1, 2]. Activities that generate wastewater include plating and electroplating industries, mining, tanning, textile, petrochemicals, and others. These activities contribute to the increase of pollutants in the environment, represent significant changes in the environment and public health management [3]. Most often, industrial effluents are characterized by the presence of various pollutants, both organic and inorganic, due to their extensive use in the chemical industry in general. These pollutants consist of microorganisms, substances with the potential to disrupt endocrine systems, phosphorus, nitrogen, and heavy metals [4, 5, 6, 7, 8]. Cr(VI) is highly migratory and readily soluble in water, considered carcinogenic and mutagenic, and harmful to the ecological environment [9, 10]. The toxic action of chromium is correlated with its valence. Hexavalent chromium Cr(VI) is toxic to all life forms and is considered a major pollutant [11]. Ecologically responsible release of wastewater requires reduction of Cr(VI) concentration up to its complete elimination [12]. In this direction, a considerable number of techniques have been developed for the elimination of hexavalent chromium from polluted waters, such as: adsorption, advanced oxidative processes, nanofiltration, reverse osmosis, ion exchange, and the use of membrane

systems. In recent years, adsorption has been shown to be an alternative method for removing metal ions from wastewater, including Cr(VI). Removal of Cr(VI) has been attempted with adsorbents such as: activated carbon [13], spirogyra biosorbent [14], fly ashes [15, 16], bentonite [17], pemza [18]. In recent years, the removal of heavy metals from wastewater has been achieved with the use of several types of natural wastes or agricultural wastes [19, 20].

#### 2. Materials and Methods

To determine the concentration of Cr(VI) ions, a spectrophotometric method (UV/VIS Spectrophotometer) type Prove 600 was used. Spectrophotometric analysis gave us the initial concentration of hexavalent chromium and the concentration after adsorption. For the spectrophotometric determination of chromium as Cr(VI), the 1,5-diphenylcarbazide method was applied as it has been validated for testing drinking and polluted waters [21]. As a working material in this research, clayey diatomite (Bitola) was used in its natural form without any treatment.

2.1. Adsorption experiment: The application of adsorption as a technique for the removal of Cr(VI) ions is very suitable and efficient. First of all, because a very high degree of removal of Cr(VI) ions is achieved, without obtaining undesirable products, and also without large capital investments.

The percentage of Cr(VI) removal is determined using the equation:

% Removal = 
$$\frac{c_0 - c_e}{c_0} \cdot 100$$

where  $C_0$  is the initial concentration of Cr(VI) ions in solution [mg/l],  $C_e$  the equilibrium concentration [mg/l].

The amount of Cr(VI) adsorbed at a given time  $q_t \lceil mg/g \rceil$  is determined by the equation:

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

where  $C_t$  [mg/l] is the metal concentration at time t [min], V [l] is the volume of the solution, and m [g] is the mass of the adsorbent.

Determining the time at which the highest percentage of Cr(VI) ion removal will be achieved is one of the most important factors. For the Cr(VI) – clayey diatomite system, the decrease in the concentration of chromium ions in solution from the initial concentration of 0.5 g/l was investigated. During the development of these experiments, data were obtained that show how the initial concentration of Cr(VI) ions decreases with time. The entire process takes place in solutions with a volume of 2l, with mixing in a magnetic stirrer with a rotation speed of 400 rpm, at room temperature and with a constant mass of adsorbent of 2.5 g/l. Samples of the solutions were taken at certain time intervals (5, 10, 20, 30, 60, 90, 120, 150 and 180 minutes), filtered, and the concentration of Cr(VI) ions in the filtrate was measured with the help of a spectrophotometer.



Figure 1. Adsorption experiment

# 3. Results and Discussion

The decrease in chromium ion concentration as a function of adsorption time with clayey diatomite is given in Figures 2, 3, 4, and 5. From the diagrams, we can conclude that in the first 10 minutes, rapid adsorption occurs and maximum efficiency in removing Cr(VI) ions is achieved.

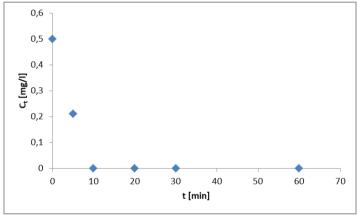


Figure 2. Change in Cr(VI) ion concentration with adsorption time for a real system groundwater, pH=2

The conditions under which the experiments were conducted are: constant room temperature, 0.5 mg/l initial Cr(VI) ion concentrations, adsorbent amount of 2.5 g/l, and pH of the solution 2.

With these experiments conducted on the influence of contact time between the adsorbent and the adsorbate, data are obtained that show how the amount of adsorbed ions increases.

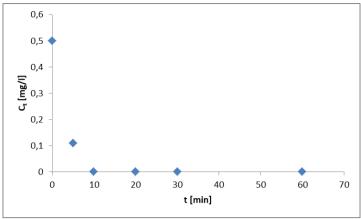


Figure 3. Change in Cr(VI) ion concentration with adsorption time for a real system surface water, pH=2

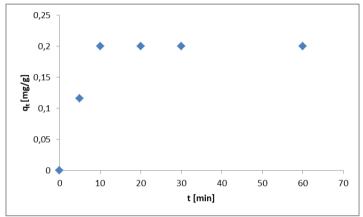


Figure 4. Dependence of the amount of absorbed Cr(VI) ions on the time of adsorption for the real system of underground water, pH=2

As can be seen, the adsorption equilibrium was reached in 10 minutes. After this adsorption time, there is almost no change in the amount of adsorbed Cr(VI) ions.

These results can also be compared with those of other authors, who have also concluded that at the beginning of the adsorption of Cr(VI) ions with different adsorbents, the process develops very quickly and by the end of the process, the concentration of chromium ions remains almost constant [22].

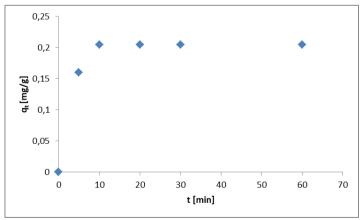


Figure 5. Dependence of the adsorbed amount of Cr(VI) ions on the adsorption time for a real system, surface water, pH=2

## 4. Conclusions

From the experimental results obtained in this research, we can conclude that: to remove Cr(VI) ions from real systems, a clayey diatomite with a granulation of 0.25 to 0.5 mm was chosen.

UV/VIS spectrophotometric analysis was used to follow the dynamics of the studied system in relation to the presence of Cr(VI) ions in real systems (UV/VIS Spectrophoto-meter).

From the graphs showing the change in concentration over time  $C_t/t$ , and the change in the amount adsorbed over time  $q_t/t$ , it can be seen that the adsorption process takes place in two phases. The rapid adsorption phase, where the largest percentage of Cr(VI) ions is removed, occurs for a period of 10 minutes, followed by a slower phase until the end of the process.

From these experimental results, we can conclude that clayey diatomite is an excellent adsorbent for the removal of Cr(VI) ions, with removal rates up to 100%. From here, we can conclude that clayey diatomite with a very low price can be used with high success as an adsorbent for the removal of Cr(VI) ions from real systems.

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