

## Removal of Cr (VI) and Cr (III) From Polluted Water and Soil Sown with Beet ( ) or Celery ( ) after the Addition of Modified Zeolites

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### Abstract

Clinoptilolite, which was modified with hexa de-cyltrimethyl ammonium-bromide solution (HDTMA-Br) in a proportion of 1/8 w/v (Z1), was applied for the adsorption of chromate anions from aqueous solutions. Different initial concentrations of chromate anions from 0 to 145 ppm were added as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to 1 g of modified zeolites adsorbent. Zeolites (clinoptilolite, Z) was also used for comparison reasons. The kinetic analysis of both adsorbents (Z, Z1) was studied at 25°C. Equilibrium isotherms of chromate anions were studied for Clinoptilolite and modified zeolites at 25, 40 and 60°C. According to the kinetic analysis, the chromate anions adsorption capacity reached at 1115.10 mg Cr (VI)/kg adsorbent for Z1 and 35.05 mg Cr (VI) kg for Z. According to isotherms, the adsorption of Cr (VI) on Z1 and Z did not increase with the increase of temperature indicating that the whole adsorption mechanism is controlled by chemisorptions and not by physical adsorption. Modified zeolites and zeolites were tested to two different soils, i.e. a soil amendments. The modification of Clinoptilolite with HDTMA-Br leads to the creation of positively charged surface sites of zeolites increasing the adsorption of Cr (VI) as chromate anions. Such adsorbents can be applied for the removal of heavy metals and dyes in an anionic form from wastewater and soil solutions where negative charged sites of Clinoptilolite present low adsorption capacity.

### Keywords

Adsorption; Clinoptilolite; Chromium; HDTMA-Br; Beet; Celery

### Introduction:

Contamination of waters and soils with heavy metal ions has become an environmental hazard due to their non-biodegradability and accumulation to living organisms [1]. One of the most abundant contaminant is hexavalent chromium, Cr (VI), which is soluble and mobile [2]. It can be leached immediately and easily stay in the groundwater and subsoil. Many industries produce effluents with high concentrations of chromium in different oxidation states during the processes of chrome plating, textile and paper manufacturing, stainless steel production, leather tanning [3,4]. The treatment of effluents before discharging them into the environment becomes necessary. One of the most promising method for the removal of contaminants is adsorption where a variety of materials were used as adsorbents, e.g. minerals, carbons.

Zeolites are present in many areas of Greece but the deposits of high financial interest are found in the following three regions, a) the province of Thrace with deposits reach in heulandites and/or Clinoptilolite, b) the islands of Kimolos and Poliegos

with deposits rich in mordenite and c) the island of Samos with deposits rich in Clinoptilolite and/or analcite [7]. Zeolites are aluminosilicate minerals quadric-charged silicon is replaced by triply-charged aluminium leading to a net negative charge of the framework. The framework is counterbalanced by cat ions such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and others placed in the cages and channels. Here positive ions can readily be exchanged with others in a bulk solution creating a unique cat ion exchange capacity (CEC). The permanent negative charge in zeolites crystal structure makes it suitable for the adsorption of cationic surfactants [9]. The ratio of Si to Al within the zeolites structure is an important factor that classifies zeolites to three categories: low Si:Al ratio (1-1.5), intermediate Si:Al ratio (2-5) and high Si:Al ratio (10 and above). Increasing the Si:Al ratio, the hydrothermal stability and hydrophilicity increases. The higher the ratio Si:Al in zeolites framework, the higher the CEC ability is observed

### Materials and Methods

Zeolites (clinoptilolite) was obtained from S and B Company. It was modified by using 0.05N hexa decyltrimethyl ammonium bromide solution (HDTMA-Br) in a proportion of 1/8 w/v (called as modified zeolites, Z1). More specifically, the mixture of Clinoptilolite and HDTMA-Br solution (0.05 N) was stirred with a magnetic stirrer for 24 h, separated by filtration and rinsed with deionised water until the electrical conductivity to fall to 53.7 µS/cm and then dried in an oven at 110°C

The adsorption ability of modified zeolites was tested using 1.0 g of Z1 and 20 ml of ten different concentrations (from 0 to 145 ppm) of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution. Samples were shaken in a water bath at 25°C for 24 h. The samples reached at equilibrium after this period and then were centrifuged at 3000 rpm for 10 min. Total chromium in the supernatant was determined using an atomic absorption spectrometer (Perkin Elmer 3300).

### Results and Discussion

The adsorbed chromium amount on each material in correlation with different time intervals is presented. It seems that Z1 adsorbent presented higher adsorption of chromate ions than Z due to the presence of HDTMA ions, which create positive charge sites in the zeolites surface. As a result modified zeolite consists of positive sites in a negative charged surface presenting simultaneously a cat ion and anion exchange capacity. Furthermore, Figure 2 depicts the adsorbed amount of chromate ions per kilogram of adsorptive material in correlation with the initial concentration of chromium at 25, 40 and 60°C.

### Conclusion

- Clinoptilolite was modified with hexadecyltri methyl ammonium- bromide solution (HDTMA-Br) in a proportion of

1/8 w/v obtaining positive surface exchange sites for the adsorption of chromate anions from aqueous solutions

- The initial Cr (VI) concentration was below 500 mg/L and the pH solution values ranged from 7.9 to 8.0 for the adsorbents indicating that  $\text{CrO}_4^{2-}$  were predominant in the solution and were adsorbed by modified 4
- The kinetic analysis has shown that the chromate anions adsorption capacity reached at 1115.10 mg/kg for Z1 and 35.05 mg/kg for Z.

### References

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