Cadmium Adsorption on Modified Turkish Clinoptilolite

Mehmet Burçin. Piskin, Ozgul. Dere Ozdemir, and Kübra. Celik

Abstract— Zeolites are crystalline aluminosilicates of group IA and IIA elements such as sodium, potassium, barium, magnesium and calcium. Nowadays, research for alternative treatment methods have an importance because of increasing of population and development of industry rapidly. Using zeolites for the adsorption of heavy metals in waste waters is advantageous method because they are strong and economic adsorbents.

In this study, removal efficiency of cadmium (Cd) from waste water by using clinoptilolite was investigated. Modification of Turkish clinoptilolite mineral was carried out with trona (Na_2CO_3) for its potential application as an adsorbent. Natural clinoptilolite has small pore sizes and low surface area compared to synthetic zeolites, modification studies have been performed to improve the sorption capacity. As a result Cd removal efficiency was 80.46% using raw clinoptilolite while 99.97% using modified clinoptilolite.

Keywords—**A**dsorbent, Characterization, Clinoptilolite, Modification

I. Introduction

RAPID industrial development in the past few decades has given rise to uncontrolled contamination of three compartments of the environment: air, water, and ground (Fig. 1). Heavy metals need a special attention among contaminants in marine environments because of their bioaccumulation in marine organisms and being conveyed through the food chain to humans. Heavy metals enter the aquatic environment mainly by direct discharges from industrial sources. Most of the heavy-metal ions are toxic and carcinogenic even at very low concentrations and usually cause a serious threat to the environment and public health [1]-[4].

Cadmium (Cd) is classified as heavy metal and a human carcinogen, widely used metal in various fields such as zinc, lead and copper smenting, electroplating, pigments, paints, alloy preparation, plastics, manufacturing, textiles, smoke detectors,electron-beam-pumped lasers, thin-film transistors and diodes mining, ceramics, and some batteries [5]-[7].

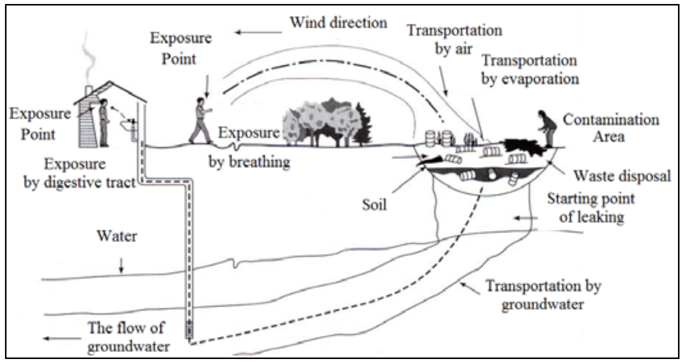

Fig.1 Hazardous wastes transportation pathways to living organism [8]

Cd has toxicological properties for human, animal and other living organism. The lungs, kidneys, bones, respitory tract, and stomach are the main target organs for chronic cadmium effects from long-term occupational exposure to cadmium [4], [6]. Since Cd is water soluble, only 1-5% of given dose is absorbed in the GI tract (although 10-40 % can be absorbed through the lungs), and Cd distributes to the kidney and liver (Fig. 2) [9].

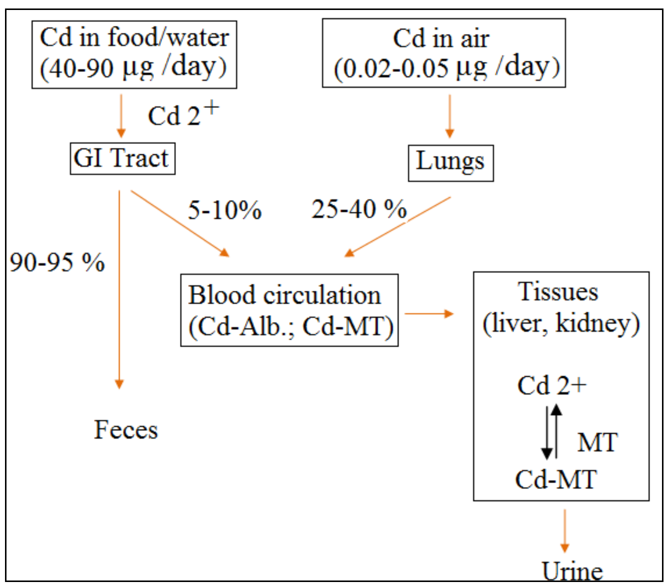

Fig. 2 Metabolism Cd in humans
(Cd-Alb: Cd attached to albumin ; Cd-MT: Cd attached to metallothionein)

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There was a terrible Cd poisoning disease in the history. Itai-itai disease (Fig. 3), is said to be one of the four major pollution-related diseases in Japan, began around the 1910s and was caused by the cadmium in the river water and rice grown on the polluted land. The cadmium was released from Kamioka Mine (Hida City of Gifu Prefecture) and it polluted the water and basin of the Jinzugawa River [10].

Fig. 3 Itai Itai patient [11]

Hence, wastewater containing Cd should be treated before discharged to environmental water bodies.

Conventional techniques including chemical precipitation, solvents extraction, ion exchange, membrane separation and adsorption can be used to remove heavy metals from wastewaters [5].

The optimization of water and wastewater purification processes requires the development of new operations based on low-cost raw materials with high pollutant removal efficiency. During the last few years, different technologies for removal of heavy metals, from wastewater such as chemical precipitation, phytoextraction, ultrafiltration, reverse osmosis, adsorption on activated carbon, and ion exchange have been used [12].

Adsorption technique is more preferable due to effectiveness and cheapness on the treatment of wastewater containing metal ions, especially, at low concentration [5]. The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently.

Natural zeolites are alumino silicate minerals with high cation exchange capacities and heavy metals selective properties. The zeolites structure consist of a three dimensional arrangement of SiO_4 and AlO_4 tetrahedral. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and isomorphous replacement of Al_3^+ for Si_4^+ results a negative charge in the lattice (Fig. 4). The net negative charge is balanced by the exchangeable cations (sodium, potassium and calcium) and these are exchangeable with certain heavy metal cations in the solution.

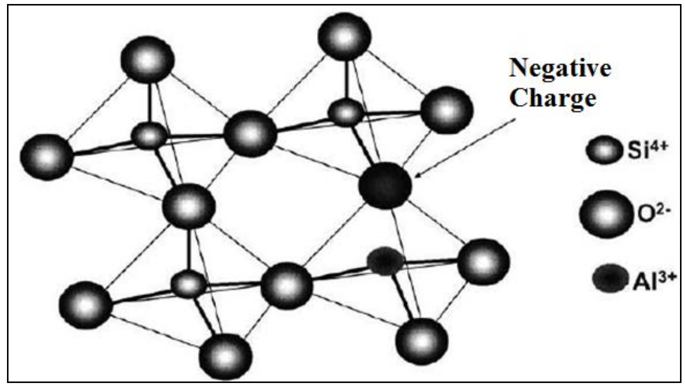


Fig. 4 Thetrahedral structure of zeolites and negatively charged thedrahedra [13]

This nature of zeolite exchangeable ions makes zeolites suitable in the remediaition of heavy metals from contaminated streams. Zeolites offer a low cost and environmentally safe method of treating minpical water supplies, domestic, industrial and mining waste water discharge [14].

Clinoptilolite has received the extensive attention due to low cost and its attractive sorption capacity for heavy metals. So its heavy metal adsorption has been investigated by many researchers. A significant number of researchers have concluded that the sorption capacity of the clinoptilolite was increased after the modification [15]-[18].

This paper presents Cd adsorption from aqueous solution by modified clinoptilolite. The scope of this study was to increase Cd adsorption percentage after modification with trona.

II. Materials and Methods

A. Materials

Clinoptilolite was obtained from Rota Mining Corporation, Gördes, Turkey. Samples were washed with distilled water and then dried at 105 °C overnight.

Trona is the most common soda minerals found in nature. It is the basic raw material used in soda ash production. In this study it was obtained from ETİ SODA AŞ., Beypazarı, Turkey.

Other chemicals are NaOH (reagent purity) for pH adjustment and Cd standard solution (Inorganic Ventures) for prepare synthetic waste water solution.

B. Zeolite Modification

Zeolite modification was carried out with Na_2CO_3 at 150 rpm. The effect of temperature, liquid/solid, concentration and time were investigated at following conditions:

Temperature: 25, 45 and 60 °C,
Liquid/solid: 1/50, 1/100, 1/200 g/ml,
Concentration: 0.5, 1, 2 M,
Time: 1, 2, 4, 6, 8, 24 h.

After this step solution was filtered and dried at 105 °C for 5 hours. General experiment flow diagram was given in Fig. 5.

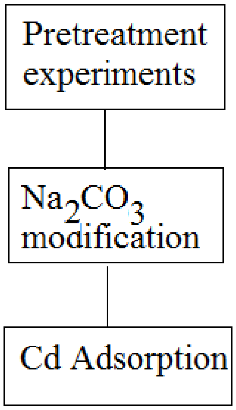


Fig.5 Experimental flow diagram

C. Adsorption of Cd from Aqueous Solution

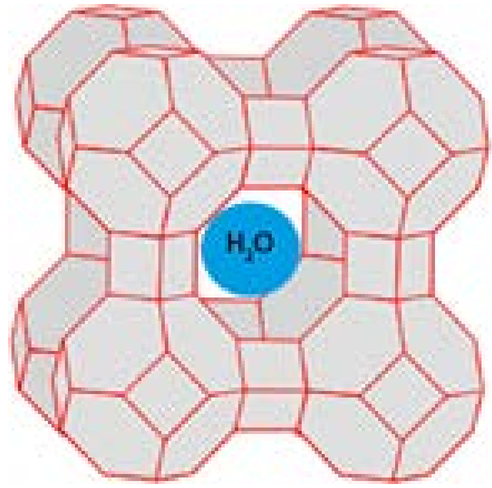
Cd adsorption from aqueous solution on modified cliloptilolite was carried out at 150 rpm, 25 °C, 1/100 solid/liquid, pH 4 for 2 hours. Initial Cd concentration was 10 ppm. Final concentrations for different conditions were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Fig. 6).

Fig. 6 ICP-OES instrument and autosampler

III. Result And Discussion

Certificated content of clinoptilolite was given in Table 1.

a)



b)

Fig. 7 Clinoptilolite a)Real image, b) Crystal structure [19]

TABLE I
CERTIFICATED CONTENT OF CLINOPTILOLITE

Compound	%
SiO_2	65-72
Al_2O_3	10-12
CaO	2.5-3.7
K_2O	2.3-3.5
Fe_2O_3	0.8-1.9
MgO	0.9-1.2
Na_2O	0.3-0.65
TiO_2	0-0.1
MnO	0-0.08

A. Effect of Modification Conditions on Cd Adsorption

Modification with trona was carried out 3 different liquid/ solid ratios. Result is given in Fig. 8. It is seen in the figure that the adsorption percentage was increased with the modification and highest result was obtained with 100/1 liquid/ solid ratios.

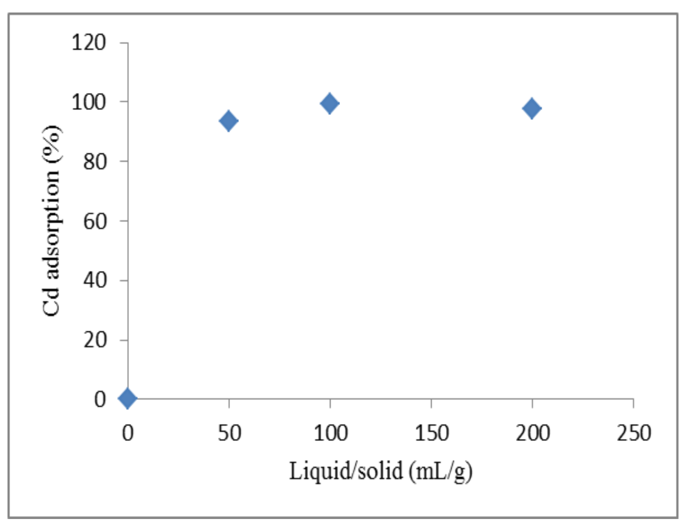


Fig. 8 The effect of liquid/ solid ratios on trona modification of clinoptilolite

Modification with trona was carried out 3 different concentrations. Result is given in Fig. 9. It is seen in the figure that the adsorption percentage was increased with the modification and highest result of Cd adsorption percentage was obtained with 1M trona solution.

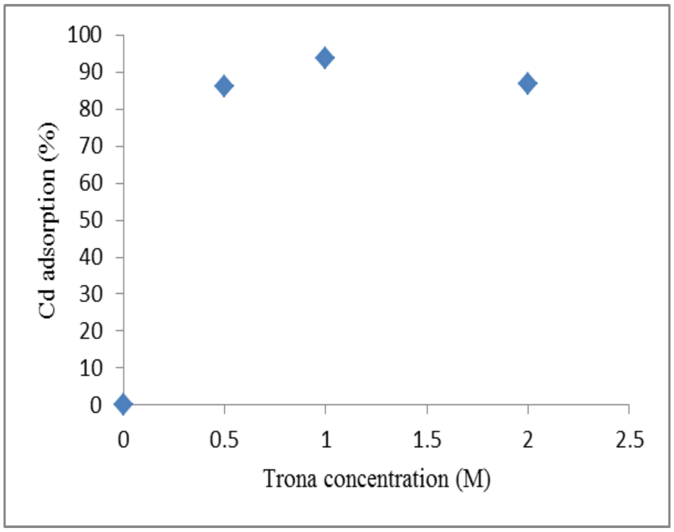


Fig. 9 The effect of concentration on trona modification of clinoptilolite

Modification with trona was performed at 1, 2, 4, 6, 8, 24 hours. Result is given in Fig. 10. It is seen in the figure that the adsorption percentage was increased with the modification time. And the adsorption percentage was constant after 2 hours.

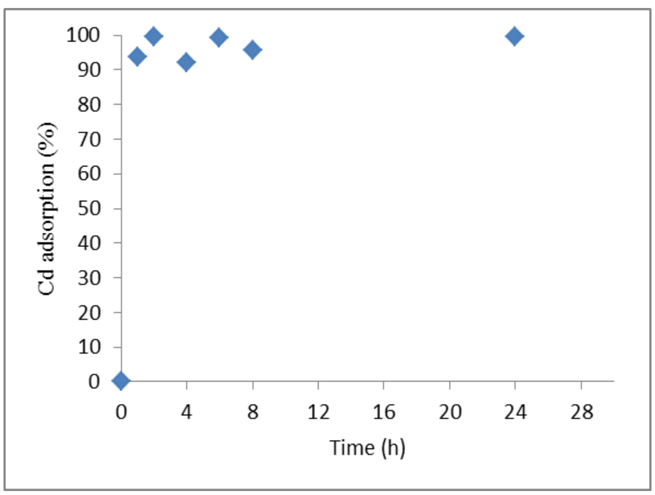


Fig. 10 The effect of process time on trona modification of clinoptilolite

Clinoptilolite modification with trona was carried out at 25, 45 ve 60 ^{o}C. Result is given in Fig. 11. It is seen in the figure that the adsorption percentage was increased with the modification and highest result of Cd adsorption percentage was obtained at 45 ^{o}C.

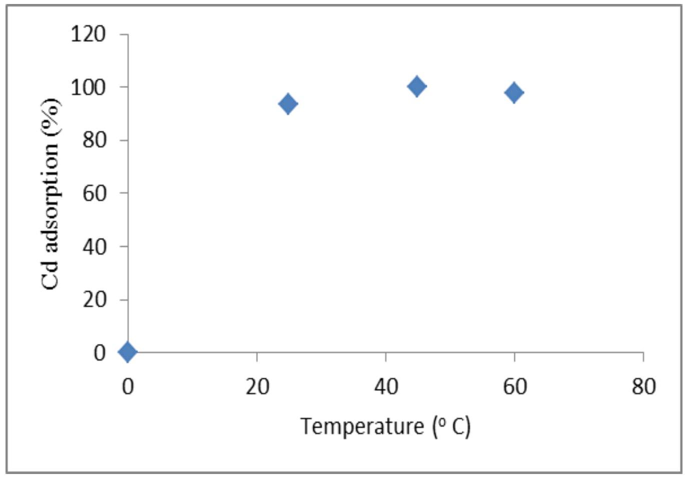


Fig. 11 The effect of temperature on trona modification of clinoptilolite

IV. Conclusion

In this study, adsorption of Cd, especially present in industrial waste waters and be a treat for environment and human health, on clinoptilolite was investigated. Clinoptilolite was used due to its low cost and naturally occurrence. Modification process was carried out with trona, natural economic mineral, in order to increase Cd adsorption percentage. The effect of different parameters on modification is investigated and the optimum conditions were found.

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