Studies Regarding Copper Recovery from Residual Solution on Naturals Zeolites

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Abstract : Chlorination is widely used to control viral contamination, high levels of chlorine promote the formation of organic compounds in water that may be hazardous to human health, an alternative method, copper ion treatment, is known to be effective against bacteria and algae. Some studies of natural zeolites have been made for their profitable use in waste treatment. The more recent use of copper ions to inactivate microorganisms is well documented. In addition to bacteria, copper ions also are effective in controlling viruses, algae and fungi in the part per billion (ppb) range. The paper relate the copper regarding from residual solutions, on natrium form zeolite. The regarding studies was done on solutions in different concentration between 55 and 500 mg Cu^{2+}/dm^3. The experimental reserch was realised in dynamic regime, and the zeolite doped with copper will be used for water disinfection.

Keywords : natural zeolites, copper, water disinfection, oligoelements

1. Introduction

Zeolites are crystalline, hydrated aluminosilicates of alkali and earth metals that possess infinite, three-dimensional crystal structures. They are further characterized by an ability to lose and gain water reversibly and to exchange some of their constituent elements without major change of structure. Zeolites were discovered in 1756 by Freiherr Axel Fredrick Cronstedt, a Swedish mineralogist, who named them from the Greek words meaning "boiling stones" in allusion to their peculiar frothing characteristics when heated before the mineralogist's blow pipe. Since that time, nearly 50 natural species of zeolites have been recognized, and more than 100 species having no natural counterparts have been synthesized in the laboratory.

Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment. They are naturally occurring alumino-silicate based minerals. Clinoptilolite is the most abundant natural zeolite that occurs in relatively large minable sedimentary deposits in sufficiently high purity in many parts of the world.[1]

The applications and potential applications of both synthetic and natural zeolites depend, of course, on their fundamental physical and chemical properties.

The ion exchange properties of zeolites and clay minerals are mainly based on the charge density and pore size of the materials.

Starting the reported research authors had in mind the importance of copper modified natural clinoptilolite systems for application in catalysis and medicine.

The Cu^{2+} ion in a zeolite framework is easily reduced and re-oxidized, involving formation of intermediate Cu^+ state. The copper (I) ions in zeolites are fairly stable, whereas the copper (II) ions supported on other amorphous or crystalline supports are readily and directly to copper (0) This might be the reason why high catalytic activity is associated with a zeolite framework structure but other supports are less reactive. [2]. The formation of large copper particles is unwelcome process that disables copper from the active state. Prevention of formation of such particles and finding out the conditions harmful for their appearance is important goal for improving of catalyst properties.

During last 15 years the discovery of new microbicide materials based on the ion exchange properties of the zeolites have been reported in literature [3-5]. The microbicide effect is attributed to the ionic state of the metals. Metal ions can be released from the zeolites by ion-exchange, because the zeolite is known to be the carrier and slow releaser of the heavy metals with olygodynamic properties. The microbicide action of copper is well established in the pharmacopoeias, also it is indispensable for life. [6]

Variation of the copper state (Cu^{2+}, Cu^+, Cu sub-colloidal and large particles) in Cu – zeolite systems might allow to regulate the release of active copper from the medical preparations. For this task the conditions of stabilizations of different states of copper should be found. Cu – containing natural clinoptilolite samples with reduced copper clusters and particles of different size are expected to be active in processes where a slow release of Cu^{2+} cations with olygodynamic properties is necessary. The ability to vary the copper bonding with the zeolite matrix, depending on preparation cations, is a critical step for modification of medical preparation properties.

Archeological excavations show, that people have been using copper for more than 11000 years. Copper can be easily extracted and processed. More then 7000 years ago people developed a copper extraction mechanism for copper ores. The Roman Empire gained most of its copper from Cyprus, the isle that gave copper its name.

Copper ions have been used for centuries for disinfecting water. The early Greeks used copper vessels to store water and Greek royalty stored water in copper flagons and drank from copper and silver goblets. The low solubility of these metals in water served as a natural controlled – release mechanism which added trace amounts of these ions to the contents of the vessel. The amounts were high enough to purify the liquid without causing objectionable taste or health problems to the users.

Copper ion disinfection of swimming pool water has several advantages over chlorine, the ions are chemically stable and do not undergo the destructive reactions of aqueous chlorine; they do not form objectionable by-products such as chloramines or trihalomethanes (THM); they do not escape from the water by volatilization as chlorine does.[8]

Copper is known to attack respiratory enzymes in bacteria, presumably by binding to groups containing, sulphydryl, amine and carboxyl moeties. Copper is also thought to facilitate hydrolysis or nucleophilic displacement reactions in peptide chains or nucleic acids. Finally, copper is able to chelate with phosphate groups and this may result in the opening of double helices.

The disease causing bacterium E. coli is killed within hours of its contact with copper surfaces, according to preliminary studies by the Center for Applied Microbiology and Research in Wiltshire, England. Scientists also are investigating whether copper plumbing could reduce E. coli found in drinking water. Based on an abundance of historical data such as the foregoing, many researchers anticipate that copper will become an increasingly important component of tomorrow's medical treatments. [7,9]

2. Experimental

This research used natural zeolite ore originated from Mirsid (Romania).

The aim of this experimental research is the retain of copper ions on the natural clinoptilolite, chemically activated in natrium form (Z-Na). [10]

It was worked with synthetic waters at different concentration, used solution of $Cu(NO_3)_2$, clean chemically reagent. Laboratory equipment it's make-up from o column with diameter by 1.5 cm, in which was introduced 10 cm^3 zeolite chemically treated (Z-Na), which granulation was 315-500 µm.

The influent with copper is passing over the zeolite Z-Na at a specifically loading of column by 10 m^3/m^3h. During the movement of the influent from top to bottom over the zeolite Z-Na, the cations are retained by ionic exchange. The column is in action until the ultimate concentration of the effluent is equal with the initial concentration of the influent.

The experimental results concerning the retention of copper on zeolite (Z-Na) for different concentration of copper in influent are presents in figure 1 - 4 for the concentration by 500 to 55 mg Cu^{2+}/dm^3.

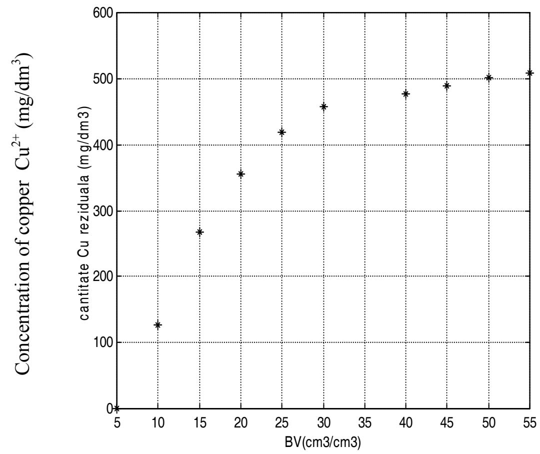

Figure 1. The dependence of copper ion from effluent function by specifically volume at concentration by 500 mg Cu^{2+}/dm^3

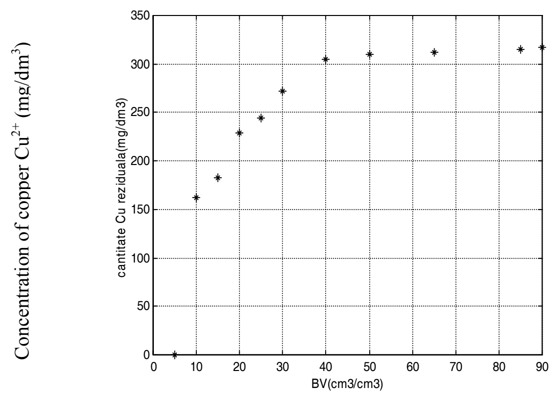

Figure 2. The dependence of copper ion from effluent function by specifically volume at concentration by 300 mg Cu^{2+}/dm^3

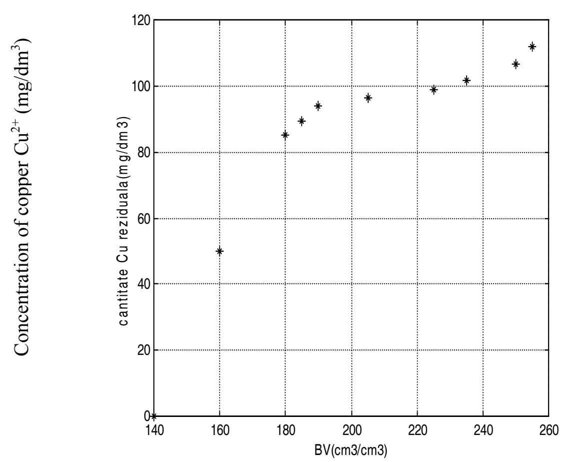

Figure 3. The dependence of copper ion from effluent function by specifically volume at concentration by 100 mg Cu^{2+}/dm^3

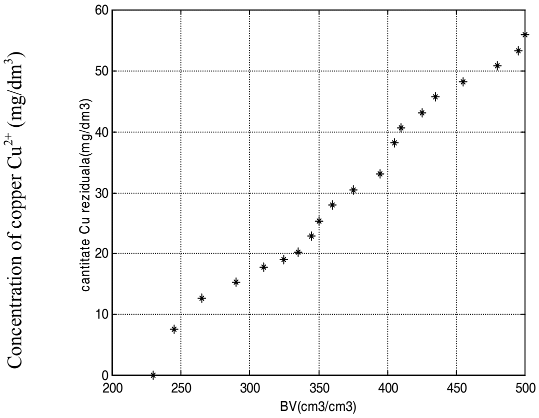

Figure 4. The dependence of copper ion from effluent function by specifically volume at concentration by 55 mg Cu^{2+}/dm^3

Experimental data processing permit to determinate the copper amount retained on zeolite, function by the influent concentration. In figure 5 are represented the retained amount of cooper.

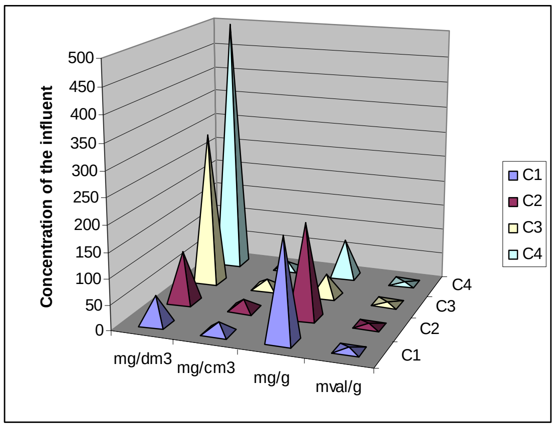

Figure 5. The dependence of copper amount (Cu^{2+}) retained by zeolite as fonction by the concentration of the influent

It was showed that at small concentration of the influent, the copper amount retained on the zeolite is bigger than the case when it used more concentrated solution.

3. Conclusions

The study in dynamic regime confirm the fact that clinoptilolitic zeolite presents selectivity for the copper ion, so it can be reclaiming from solution residue with the view to obtaining the zeolite doped with copper.

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