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THE EFFECTIVENESS OF ZEOLITE FOR THE REMOVAL OF HEAVY METALS FROM AN OIL INDUSTRY WASTEWATER

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Abstract. Batch experiments are applied to determine the effectiveness of zeolite addition on the characteristics of wastewater of the oil industry and operational factors. The concentrations of heavy metals were measured using an atomic absorption spectrophotometry. Results have shown that 2.5 g/L of zeolite at a speed of 270 rpm, 6.5 pH would result in about 99% removal efficiency.[1]

Keywords: heavy metals, oil industry, wastewater, zeolite.

1. Introduction

The presence of toxic heavy metals in groundwater brings major changes in the characteristics of water resources and must be avoided in order to maintain the quality of the environment. These minerals can be related to numerous human sources and highly toxic compounds. Many heavy metals, such as mercury, chromium, cadmium, accumulate in aquatic food web access to humans through the food chain and cause many diseases. At present, the population of the world, along with the accelerated technological progress and the accompanying environmental pollution/climate change, lead to a drastic reduction in the availability of water resources and the deterioration in water quality.[1] There is a number of factors to blame, and the most important of which is the massive water control projects in the source river locations that cause scanty precipitation because of climate change. In many countries, groundwater is generally more reliable than surface water. For example, in the United States, 56 % of the population relies on groundwater for drinking. However, groundwater resources are vulnerable to any easily soluble chemical element that can penetrate the soil.[2] Chlorinated hydrocarbons and heavy metals which are the most dangerous pollutant threats continuously released into groundwater as a result of many industrial processes and waste disposal. The objective of this work is to study the possibility of the application of zeolite to remove cadmium from contaminated groundwater.

Zeolite is defined generally as aluminum owning 3D frameworks linked to tetrahedron silicon and aluminum and oxygen. Analog replacement of Al_3^+ Si_4^+ results in a negative charge imbalance in lattice zeolite which is balanced by cations, usually hydrated Na^+, K^+ and Ca_2^+ in nature. This means high scalability for cations such as heavy metals and minerals, but low affinity for anions and organic non-polar compounds.[3] The study is adopting commercial pellets of zeolite (35.96 mm diameter), that is manufactured by D-wax company for synthetic zeolite, washed with 1M resins of sodium hydroxide and 1M hydrochloric acid so as to remove organic impurities, and then to be washed with distilled water that would remove other impurities. The Table illustrates the physical and chemical properties of zeolite.

Table. Composition and physico-chemical properties of zeolite

Properties	Values
Composition, wt %:	
SiO_2	34.48
Al_2O_3	29.94
Na_2O	13.4
CaO	2.52
TiO_2	1.7
LOI, wt%	15.05
Bulk density, g/cm^3	0.58
Particle density, g/cm^3	1.2
Porosity, %	0.34
Surface area, m^2/g	1000
Cation exchange capacity, meq/100g	1.8

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2. Experimental

A series of batch tests were designed in order to determine the proper amount of zeolite to reduce the concentration of lethal heavy metal contaminants (Cd, Zn, and Pb) in oil industry wastewater. The governing parameters such as contact time, pH, initial contamination, agitating speed and dose of resin were to be tested for the best removal performance. Batch scale experiments would involve the use of an atomic absorption spectrophotometer (Norwalk, Connecticut, USA), in order to measure the concentration of soluble cadmium. pH Meter is used to measure the pH of the aqueous solution and the agitating speed would be achieved *via* a high-speed orbital agitator with an adjustable agitating speed of 150, 200, 250 and 270 rpm. Batch tests were conducted to determine the best operational conditions that would result in the best removal efficiency.

3. Results and Discussion

Ion exchange is generally a relatively rapid process, the time to reach equilibrium in batch systems is usually found to be less than 1 h, although it can be up to 2 h. While the change in the properties due to the addition of zeolite affects the ion exchange and the operational conditions including the time to reach equilibrium in batch tests [4]. Fig. 1 shows the Cd removal efficiency along with the contact time with the use of 0.25 g of zeolite that was added to 100 ml of metal solution for batch tests at 298 ± 1 K. The removal efficiency increases sharply during 25 min up to about 85 %, due to the vast availability of targeted adsorbate for the ion exchange process.[5,6] Beyond that, the efficiency increased in a moderate manner until the end for about 60 min, when about 97 % of the initial Cd contaminant was removed, while few minutes after that 99 % efficiency was recorded.

As metal ions pH value plays an important role at the protonation and deprotonation of acidic and basic set reaction in the absorption process, due to its effect on the surface texture of absorbent materials, forming hydroxides minerals,[7] the pH dependence of absorption was investigated for metal ions in detail. The Cd absorption process by 2.5 g/L zeolite as a function of time was tested for a pH range of 2–8 at an initial ionic concentration of 50 mg/L and an agitating speed of 270 rpm. The results of these tests are demonstrated in Fig. 2, which proved the high sensitivity of metal ions absorption behavior to the changes in pH. It has been observed a significant increase in the absorption of Cd by increasing the pH of the solution up to 6.5. No hydroxy complexes in the solution at pH less than 6.5 as merely ion water formation of Cd^{2+} ions are present. Accordingly, the increase in metals due to the pH increase (solution goes more basic) may be attributed to the basis of reduced competition between proton and metal types of surface sites and lower positive surface charge, which leads to a columbic diss-harmony that is less than the metal adsorbate. However, further increase in pH value caused a reduction in the removal efficiency, which might be caused by the formation of negative cadmium hydroxides $(OH)^{2-}$ that precipitated from the solution. In addition, at low pH values an excess of protons competes effectively with Cd^{2+} ions with the sites on the surface of the zeolite bound. This effect is due to the surface low-affinity starting from the high-affinity to reach saturation, leading to a decrease in the removal efficiency.

The effect of the initial contaminant (Cd) concentration on the final removal efficiency was tested under fixed operating conditions; the solvent amount of 100 mL, zeolite dose of 0.25 g, 60 min contact time and pH of 6.5. This set of tests showed that a slight reduction occurred in the final removal efficiency – from 99 to 96%, as the initial contaminant concentration was raised from 50 to 100 mg/L (Fig. 3). This reduction was highly significant with the increase of the initial Cd^{2+} concentration up to 200 mg/L, where the removal efficiency was dropped to about 55 %. A slight reduction in the removal efficiency was recorded as a result of the increase in the adsorbed metal ions from 200 to 250 mg/L. This is interpreted as the number of metal ions adsorbed per unit mass of zeolite in a balance/suction was rapidly decreasing in the initial metal ions concentration and then began slightly decrease with the increasing concentration of metals in aqueous solutions between 200 and 250 mg/L. The results are in an agreement with those represented by Olabemiwo *et al.*[8]

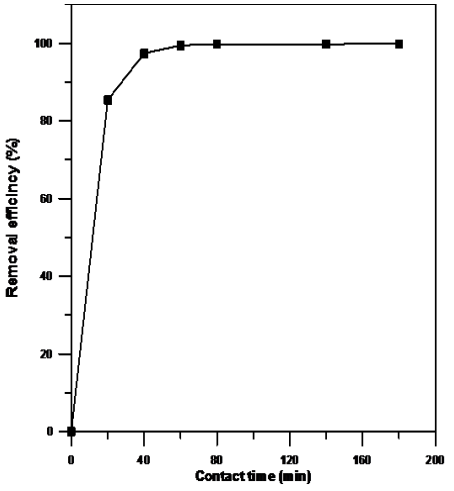

Fig. 1. Cd removal efficiency of zeolite as a function of contact time (pH = 6.5; zeolite dose = 2.5 g/L; speed = 270 rpm; T = 298±1 K)

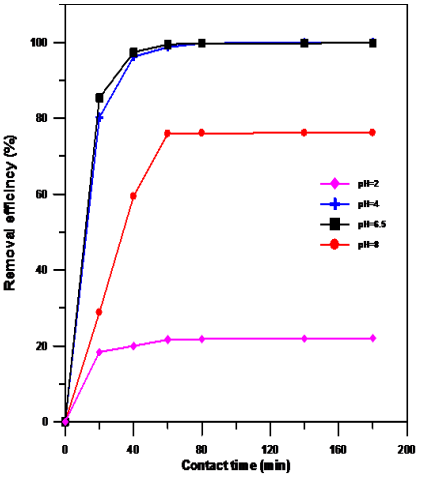

Fig. 2. Effect of initial concentration on removal efficiency of Cd (pH = 6.5; zeolite dose = 2.5 g/L; speed = 270 rpm; contact time = 60 min; T = 298±1 K)

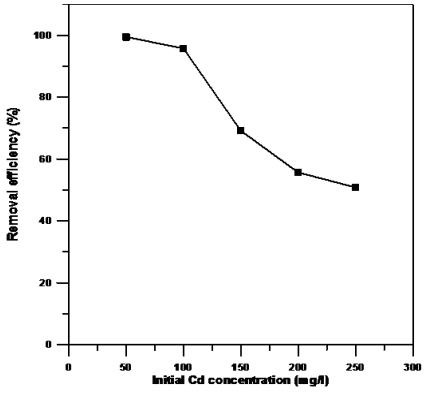

Fig. 3. Effect of initial concentration on Cd removal efficiency (pH = 6.5; zeolite dose = 2.5 g/L; speed = 270 rpm; contact time = 60 min; T = 298±1 K)

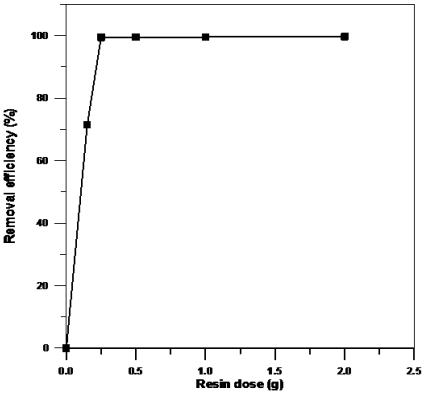

Fig. 4. Effect of resin dosage on Cd removal efficiency (pH = 6.5; speed = 270 rpm; contact time=60 min; T = 298±1 K)

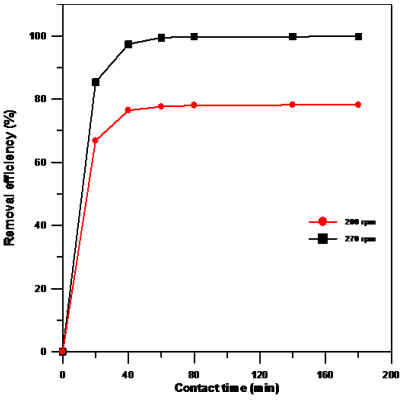

Fig. 5. Effect of agitation speed on Cd removal efficiency as a function of contact time (pH = 6.5; resin dose = 2.5 g/L; T = 298±1 K)

The effective zeolite (resin) dose to be used for achieving the highest removal efficiency was determined *via* the set of experiments demonstrated in Fig. 4, that proved rapid efficiency increase as a result of the increase of zeolite up to 0.25 g into 100 mL of a solvent, 2.5 g/L, due to the higher dose of adsorbent in the solution, and the availability of more adsorbate. No significant improvement was detected with a more increase of the zeolite dose.

The impact of agitating speed on the final removal efficiency was also tested in a separate set of experiments, the results of which are illustrated by Fig. 5. They proved that a maximum of about 77 % of Cd ions was removed with an agitating speed of 200 rpm after 60 min, which was remarkably low as compared to 99 % with the 270 rpm agitating speed under similar operating conditions, in the past sets of experiments. These results can be linked to the fact that the increase in the metal ions deployment speed improves the excitement towards the surface of the capacitor at fast agitation, metal ions soaked up to the top, hence assure that all sites would be available for the adsorption process.[9]

4. Conclusions

Series of consequent batch scale laboratory designed experiments were made to examine the impacts of various governing parameters on the adsorption effect

of zeolite on the contaminant heavy metals in the wastewater of oil industry. These parameters were: the zeolite (resin) dose, initial contaminant concentration, agitation speed, contact time and the pH value. The overall results proved that zeolite may serve as an excellent adsorbent that can remove almost all the contamination of heavy metals (adsorbate). A resin dose of 2.5 g/L, would result in about 99 % Cd removal efficiency from the wastewater that includes Cd contaminant of up to 50–100 mg/L under an ambient temperature of 298 ± 1 K after 60 min of agitation with a speed of 270 rpm and the solvent pH of 6.5. The increase of zeolite dose, contact time, and the agitation speed was proved of no significant impact on the final removal efficiency; whether positive or negative. On the contrary, the increase of the solvent pH was found to negatively affect the final removal efficiency. Also, a comparable reduction of the removal efficiency was determined to occur with the increase of the initial heavy metals concentration by more than 100 mg/L.

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ВИЗНАЧЕННЯ ЕФЕКТИВНОСТІ ЦЕОЛІТУ ДЛЯ ВИДАЛЕННЯ ВАЖКИХ МЕТАЛІВ ІЗ СТІЧНИХ ВОД НАФТОВОЇ ПРОМИСЛОВОСТІ

Анотація. *Проведено комплексні дослідження для визначення ефективності цеоліту щодо покращання характеристик стічних вод нафтової промисловості. За допомогою атомно-абсорбційної спектрофотометрії визначено концентрації важких металів. Встановлено, що цеоліт у кількості 0,2 г/л, за швидкості 270 об/хв і pH 6,5 дає можливість досягти ефективності видалення металів приблизно 99 %.*

Ключові слова: *важкі метали, нафтова промисловість, стічні води, цеоліт.*