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ANIONIC DYE REMOVAL FROM AQUEOUS SOLUTION USING CHITOSAN - MODIFIED IRIND MINE PUMICE

In this paper, the adsorption of Congo red dye from an aqueous solution using chitosan-coated pumice (CCP) has been studied. The abundant natural pumice from Irind mine (Republic of Armenia) was successfully activated by an acid activation method and modified with chitosan. The adsorbent was applied as a low-cost, and environmentally-friendly adsorbent for Congo red dye removal from aqueous solution. The modified pumice samples were characterized by Fourier-transform infrared spectroscopy (FT-IR). To study the adsorption behavior of Congo red dye on modified pumice, the batch adsorption method was used. The effects of operating parameters on Congo red dye adsorption on modified pumice were examined, including adsorbent dose, pH, contact time, and starting concentration. Solutions of Congo red dye concentrations before and after adsorption were measured by UV-Vis Spectrophotometer (Cary-60). The wavelength of 3.799 nm^{-1} corresponds to the dye's maximum absorbance, and the obtained spectra revealed that no peak was found above the threshold after modifications.

Keywords: *surface-modified pumice, chitosan, Congo red dye, absorption.*

Introduction

The presence of dye in water has a negative impact on all living organisms. The textile industry plays a pertinent role in dye emissions into the ecosystem. Of several natural and synthetic dyes, azo group proliferation has been highly carcinogenic due to amine and benzidine emissions. In addition, the fact of being non-biodegradable makes the dye molecules last longer in the environment, producing hazards. Commonly, dyes used in the textile industry are synthetic with high resistance to oxidizing agents, biodegradation, and photo-degradation treatments [1]. Congo red dye is one of the most common synthetic dyes used in the textile industry. They are a class of benzidine-based anionic diazo dyes with high toxicity and irritant properties for eye and skin contact (Fig.1).

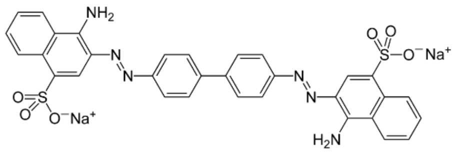

Fig. 1. *Chemical structure of Congo red dye*

At a high level of contamination, it could induce some respiratory problems and could even be carcinogenic to humans. Consequently, Congo red dye removal from wastewater is a necessity to avoid environmental issues. Various technologies have been developed to remove dye contamination from wastewater, including filtration, coagulation, electrochemical oxidation, chemical oxidation, membrane filtration, and adsorption [2].

Among all the above mentioned techniques, adsorption is considered the most feasible method to remove dye contamination in aqueous conditions [3,4]. Adsorption is a well-known separation method of high effectivity for water contaminant removal. Because of its simplicity, adsorbent reuse capability, insensitivity to harmful pollutants, high efficiency, and low cost, adsorption looks to be the most efficient technology currently available.

With its abundance and diversity of non-metallic minerals, the Republic of Armenia leads worldwide. In this study, Irind mine pumice is used as an adsorbent. Irind is located in the Talin region. It is 46 km away from the regional center. There are perlite and pumice resources in the village, which are of industrial importance. Pumices in Armenia are classified into two groups based on their physical-mechanical characteristics: Ani pumices and lithoid pumice. The Irind mine pumice is one of the Ani-type varieties. Ani-type pumice is mainly composed of glass non-crystalline (amorphous) particles: plagioclase, pyroxene and mineral crystals, and pieces of old lava. The color is yellowish, sometimes yellow-brown or pink-yellow, and the porosity is 35–44%. It has high thermal insulation properties. The bulk density of the pumice is 0.3-0.6 g/cm^3.

Studies have shown that the pumice is composed of alumosilicates in which the amount of alkaline oxides are: SiO2 -61.54 %, MgO - 1.13%, TiO2 - 1.00%, Fe2O3 - 3.99%, K2O +Na2O - 8.18 %, Al2O3 - 16.58%, and CaO is 3.78 % [5].

The examination of the pumice by X-ray diffractometry have shown that it is a volcanic rock and is composed of cristobalite and coesite. Coesite and cristobalite are high-pressure polymorphs (crystal form) of silica (SiO2). They have the same composition but possess a different crystal structure [6].

Today, many methods have been studied to increase the adsorption capacity of natural pumice for contaminants removal from wastewater. Commonly, the materials can be modified by both physical and chemical treatment. Pumice chemical modification has changed the nature of pumice as an adsorbent for dye removal from aqueous solutions. In this study, the abundant natural pumice was activated using HCl and was modified with chitosan. Chitosan is a versatile polysaccharide widely distributed in nature (second most abundant biopolymers after cellulose) produced by alkaline N-deacetylation of chitin (Fig.2).

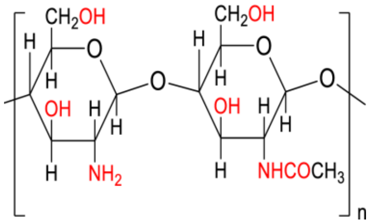

Fig. 2. *Chemical structure of chitosan*

Many application fields are described in scientific publications regarding the use of chitin, chitosan and their derivatives. Wastewater treatment using chitin or chitosan is an important application. According to this, there are many research studies that highlight the biosorbent ability of chitosan and their composites to remove pollutants from wastewater. They could be used as coagulating/flocculating agents for polluted wastewaters [7], in heavy metal or metalloid adsorption (Cu (II), Cd (II), Pb (II), Fe (III), Zn (II), Cr (III), etc.) [8, 9], and in the removal of dyes from industrial wastewater [10].

Pumice with grain sizes from 1 to 2.5 mm were used for the experiment. The materials were first ground, washed with running tap water to remove impurities, and rinsed with distilled water. Then, they were treated with 0.1 M HCl for two, three, four, and five hours. The optimal time was chosen for three hours. After three hours of acid treatment, the materials were washed with distilled water to remove excess acid until the pH of the washing water was equal to that of distilled water. The washed materials were oven-dried at 60^{o}C for four hours to evaporate the remaining water. For modification of pumice surface the powder was added to 100 ml of 3 percent acetic acid, where 3g of chitosan was dissolved. The mixture was left for 24 hours, after the pumice was filtered, washed with distilled water, and dried in an oven at 60^{o}C for 5 hours.

Results and Discussions

Fourier transforms infrared (FT-IR) spectra of the chitosan films and the chitosan/pumice films were plotted using a Thermo Nicolet AVATAR 330 FT-IR spectrophotometer (Thermo electron corporation).

FT-IR analysis of (pumice) and chitosan coated pumice was performed in order to describe the functional groups responsible for the binding mechanism between the adsorbent and the coated sample. The changes arise during the coating of pumice as presented in the Fig. 3. The FT-IR spectrum of CCP shows a predominant broadband around 2921 and 2852 cm^{-1} assigned for asymmetric and symmetric stretching vibration of CH groups. A functional groups like –C=O, –COO were found at wave number intervals of 1626 and 1457cm^{-1}. Absorption band in the range of 1627–1450 cm^{-1} was ascribed to the vibration of carbonyl bonds (C=O) of the amide group CONHR (secondary amide) and the vibration of the protonated amine group. The limited peak at 515 cm^{-1} correlates to oscillating of the saccharide structure of chitosan [11].

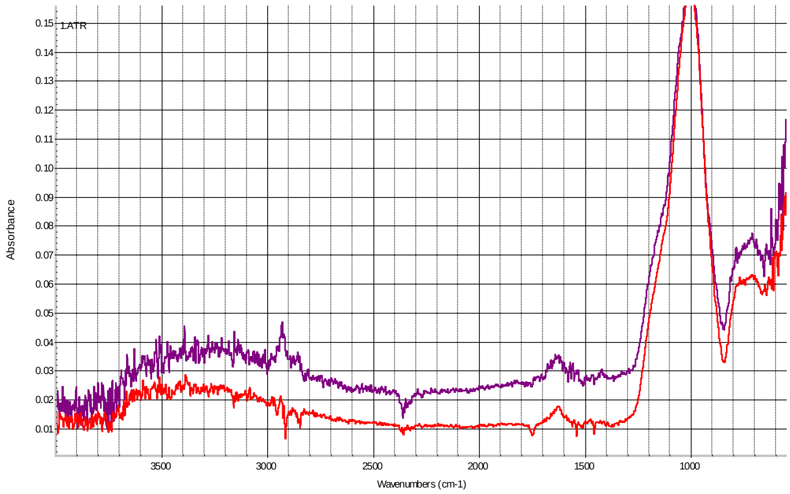

Fig. 3. *FT-IR spectra of pumice modified with chitosan (— - pumice, — - chitosan coated pumice)*

The Congo red dye adsorption tests were carried out in batch experiments by adding 1 g of an adsorbent. Typically, 0.5 g of pumice was added to a 100 ml flask containing 50 ml of Congo red dye solution at the predetermined concentration. As one of the diazo class dyes, the form of the Congo red dye molecule in the aqueous solution will be affected by the pH value. As mentioned in [12,13], the color of Congo red dye changed significantly from red to dark blue when the pH of the solution was reduced to 2. On the other hand, when the pH of Congo red dye solution was adjusted to be more than 10, its color was different from the original. Hence, in this work, the effect of the initial pH solution on the adsorption of the Congo red dye on pumice was studied at pH ranging from 3 to 9 for an initial concentration of Congo red dye of 100 mg/L. The results indicate that the adsorption of Congo red dye on the pumice was affected by the pH of the solution. The most favored adsorption process occurred at a pH of 3.9. The Congo red dye concentrations before and after adsorption were measured using UV-Vis Spectrophotometer (Cary-60). The wavelength of 3.799 nm^{-1} corresponds to the maximum absorbance of the dye. The spectra show that no peak was observed over the threshold after modification (Table, Fig. 4).

Table. UV-Vis absorbance report

Instrument parameters		Sample name (pumice)	Data before modification
Instrument	Cary 60	Peak Style	Peaks
Instrument Version	2.00	Peak Threshold	0.0100
Start (nm)	800.0	Range	800.0 nm to 200.0 nm
Stop (nm)	200.0	Wavelength (nm)	Abs
X Mode	Nanometers	205.0	3.785
Y Mode	Abs	203.0	3.799
UV-Vis Scan Rate (nm/min)	600.000		
UV-Vis Data Interval (nm)	1.00		
UV-Vis Ave. Time (sec)	0.1000		

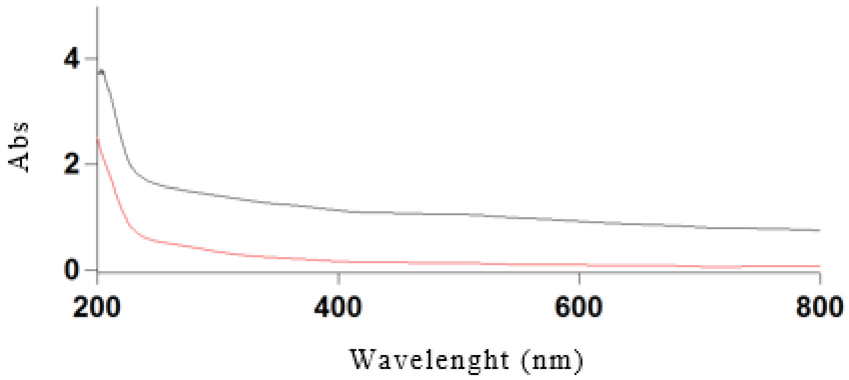

Fig. 4. *UV-Vis Spectrophotometer data*

Conclusion

The capability of acid-activated and chitosan-modified Irind mine pumice to absorb Congo red dye from aqueous solutions was studied. The characterization of the natural pumice sample before and after surface modification with chitosan showed that the structure of the natural pumice was successfully modified. The Congo red dye adsorption tests were carried out in batch experiments by adding 1 g of an adsorbent. The results show that the pH of the solution influenced the adsorption of Congo red dye on pumice. The most favored adsorption process occurred at a pH of 3.9. The Congo red dye concentrations before and after adsorption were measured using a UV-Vis Spectrophotometer (Cary-60). The wavelength of 3.799 nm^{-1} corresponds to the maximum absorbance of the dye. After modification, no peak was found above the threshold.

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