RESEARCH ARTICLE

Modification of Clinoptilolite Zeolite for Nitrophenol Removal from Aqueous Solutions

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ABSTRACT

Among the methods for removing organic pollutants, adsorption is an efficient and effective process due to its low cost, ease of operation, and high efficiency. The use of mineral adsorbents, especially zeolites, has received special attention due to their appropriate adsorption capacity and selectivity, high stability (even at high temperatures), low cost, and effectiveness. This research aimed to investigate the performance of clinoptilolite zeolite modified with the cationic surfactant hexadecyl trimethylammonium bromide as an adsorbent for the removal of 2, 4-dinitrophenol from aqueous solutions. The analysis of this pollutant was performed using a UV-Vis spectrophotometer at the maximum absorption wavelength (360 nm). Scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR) were used to investigate the properties of the synthesized adsorbent. The most important laboratory variables, such as initial pollutant concentration, contact time, temperature, adsorbent amount, and pH, were investigated to increase the adsorption efficiency.

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INTRODUCTION

Nitrophenol compounds are among the most common compounds that can enter the environment from industrial wastewater and reduce the quality of receiving water resources. These compounds are widely used in the pharmaceutical, textile, dye, rubber, pesticide and explosive industries and ultimately enter water resources through industrial wastewater. Due to the negative effects of this group of compounds on human health and the environment, the US Environmental Protection Agency has classified nitrophenol compounds as priority pollutants and has called for the reduction of the concentration of this group of compounds in natural waters to less than 10 ($ng.L^{-1}$). According to studies, one of the most toxic and resistant compounds in this group is 2, 4-dinitrophenol (2,4DNP) [1, 2]. 2, 4-dinitrophenol, with the chemical formula $C_6H_4N_2O_5$, is a cyclic hydrocarbon with a molecular weight of 184.106 ($g.mol^{-1}$). It is a yellow crystalline solid with a sweet,

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musty odor. It sublimes readily and is soluble in most organic solvents as well as aqueous alkaline solutions [3]. Nitrophenol (NP) pollutants, including 2, 4-dinitrophenol (DNP), pose a significant threat to environmental and human health due to their persistence, toxicity, and endocrine-disrupting effects in aquatic ecosystems [4, 5]. DNP is a specific nitrophenol derivative known for its severe health consequences, historically misused as a weight-loss agent, and remains a concern due to accidental poisonings [6, 7]. Both DNP and other NPs are harmful pollutants that can contaminate water sources through various industrial activities, posing challenges for remediation efforts [8, 9]. Zeolites are a fascinating class of naturally occurring microporous aluminosilicate materials generating considerable interest in various scientific fields due to their unique properties and diverse applications [10, 11]. Their well-defined crystalline structure, characterized by a tetrahedral framework of silicon (Si) and aluminum (Al) oxides linked by oxygen atoms, creates a network of uniform pores [12, 13]. This structure grants zeolites exceptional adsorption, ion-exchange, and catalytic properties, making them highly versatile materials for numerous industrial and environmental applications [14, 15]. By changing the particle size of zeolites from micrometers to smaller scales such as nanoscale, the capacity is increased and the kinetics of the adsorption process is also significantly increased. The ratio of silicon to aluminum, volume, size and shape of pores and channels in the zeolite structure are effective for the adsorption of pollutants [16, 17]. Within the zeolite family, a wide variety of frameworks and compositions exist, each exhibiting distinct characteristics and functionalities [18, 19]. In Iran, approximately 40 types of natural mineral zeolites have been identified. Since zeolites from different locations have different impurities, they do not exhibit the same adsorption behavior. Clinoptilolite zeolite with the chemical formula $Na_6 (AlO_2)_6(SiO_2)_{30}.24H_2O$ has a high ion exchange capacity and a large internal and external surface [20]. Clinoptilolite (clinopt) is one of the most abundant and commercially relevant natural zeolites, attracting significant research attention due to its particular properties and potential applications [21, 22]. Cetyltrimethylammonium bromide (CTAB) with the formula $(C_{16}H_{33}) N (CH_3)_3Br$ is one of the common compounds used as a disinfectant. This cationic surfactant is a disinfectant against bacteria and fungi. It is used as a buffer solution for DNA extraction and is also widely used in the synthesis of gold nanoparticles [23].

EXPERIMENTAL

Materials and methods

All chemicals and solvents were purchased from Merck. Clinoptilolite zeolite (ZoC) was obtained from Protech Minerals, LLC (USA). A Perkin Elmer Lambda 25 UV-Vis spectrophotometer (USA), a Panalytical X pert pro X-ray diffractometer (XRD) (England) and a Jasco 410 FT-IR spectrometer (Japan) were used for characterization. The morphology of the nanoparticles was studied using a ZEISS SIGMA VP-500 scanning electron microscope (SEM) (Germany).

Preparation and Modification of Zeolite

500 g of clinoptilolite zeolite (natural zeolite) was sieved with the finest sieve available (mesh No. 18, hole size 1 mm), washed with distilled water 5 times, and dried in an oven at 80 °C for 6 hours. Then, 5 g of zeolite was treated with 100 mL of 1 M NaCl for 4 hours at 2000 rpm on a shaker. The supernatant was decanted, washed with distilled water 3 times, dried in an oven at 80 °C for 5 hours, and added to a beaker with 0.5 g of CTAB surfactant and 100 mL of distilled water. The beaker was placed on a shaker at 40 °C for 15 hours. The contents of the beaker were then filtered through filter paper. The resulting solid surfactant was washed with distilled water and dried in an oven at 60

°C for 6 hours. The prepared ZoC/CTAB was placed in a desiccator.

Optimization of Parameters Affecting Adsorption

The effect of pH, temperature and contact time on adsorption was investigated and the optimal amount of each factor was determined.

RESULTS AND DISCUSSIONS

Characterization of adsorbents

FT-IR analysis

The FT-IR spectrum of the CTAB-modified clinoptilolite zeolite is shown in Figure 1. The adsorption peaks for CH_2 vibrations in the CTAB molecule were observed at 2912 (cm^{-1}) (asymmetric vibrations) and 2847 (cm^{-1}) (symmetric vibrations), respectively. The peaks appearing at 3057 (cm^{-1}) and 1000 (cm^{-1}) are attributed to CH_3-N and C-N vibrations, respectively, while the bending vibrational bands of the methyl group [N $(CH_3)_3$] appeared at 1456 (cm^{-1}) and the stretching vibrations of CN appeared at 1028 (cm^{-1}).

SEM analysis

The SEM analysis of the ZoC/CTAB adsorbent is shown in Figure 2. The particles have a cubic structure, indicating that the zeolite structure has not changed after modification. Upon modification of the zeolite, only particle aggregation has occurred, which is due to the presence of the surfactant on the surface of clinoptilolite zeolite. The pores present in the zeolite structure are also completely filled with surfactant molecules after modification.

XRD analysis

Structural analysis of zeolite using XRD technique revealed that the main component present in the structure of this adsorbent is quartz (SiO_2). Adsorbent is also composed of CaO, Al_2O_3, K_2O, Na_2O, Fe_2O_3, and MgO.

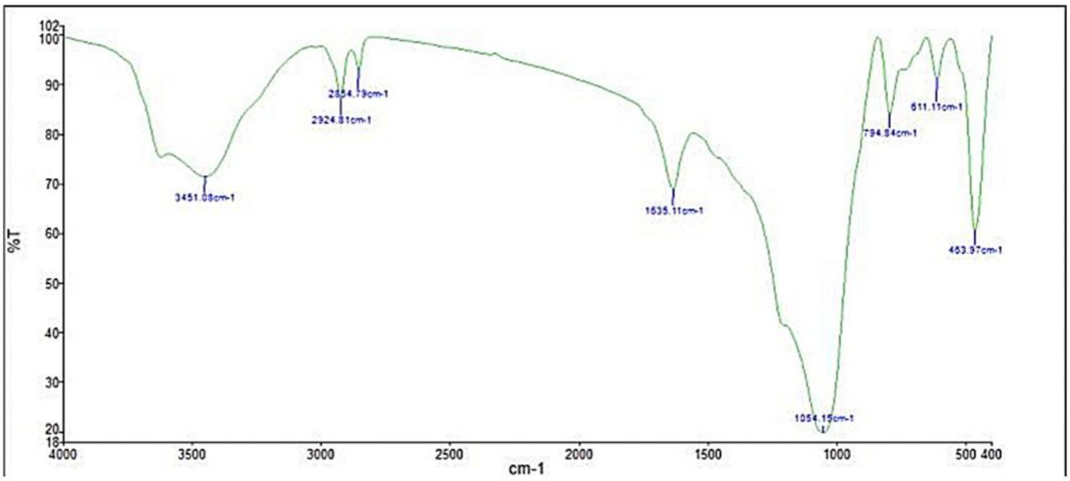

Fig.1: FT-IR spectrum of the CTAB-modified clinoptilolite zeolite

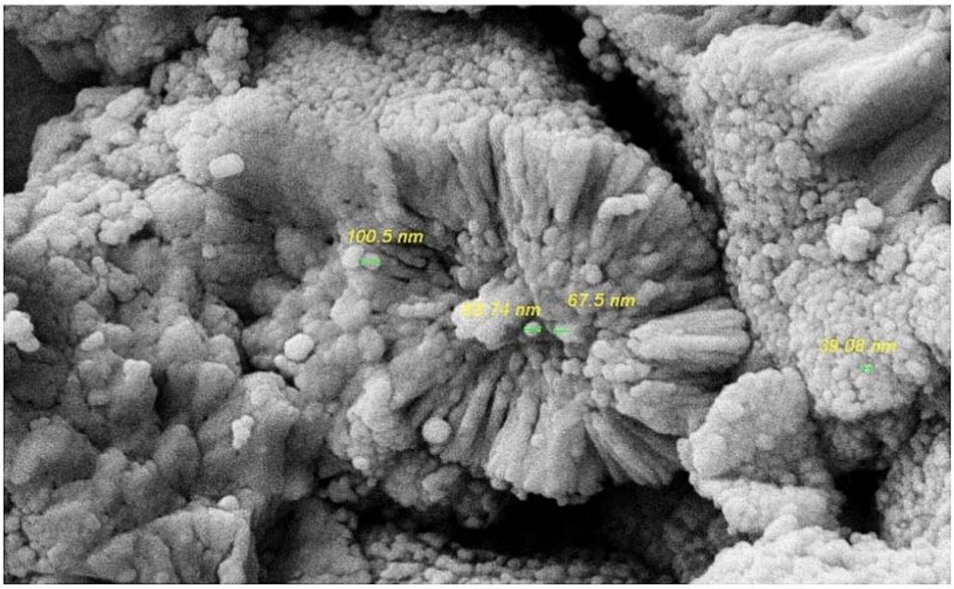

Fig.2: SEM analysis of ZoC/CTAB adsorbent

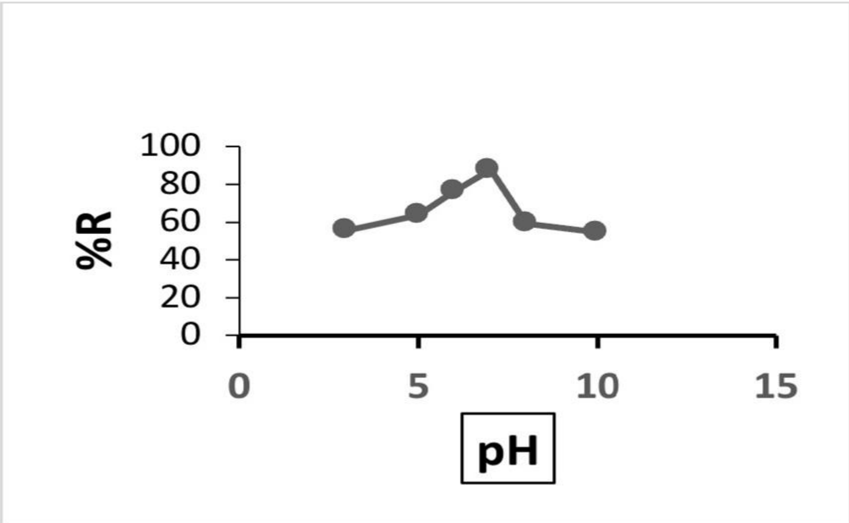

Fig.3: Effect of pH on adsorption efficiency by ZoC/CTAB adsorbent

Optimization

The effect of pH

The percentage adsorption at pH values between 3 and 10 is shown in Figure 3. The highest adsorption of 2, 4-DNP was obtained at pH=7. As the pH increased from 3 to 7, the percentage adsorption increased significantly from 55% to 87%. However, as the pH increased from 8 to 10, the percentage adsorption of 2,4DNP on ZoC/CTAB decreased to 54%.

The effect of temperature

The results obtained from the temperature change and its effect on 2,4DNP removal showed that the removal efficiency of 2,4DNP pollutant decreases with decreasing temperature and shows its best performance at room temperature. Increasing the temperature causes the destruction of the pollutant and the adsorbent, resulting in a decrease in the removal .efficiency

The effect of contact time

The percentage removal increased with increasing contact time between the adsorbent and 2, 4- DNP.

CONCLUSION

The results of the investigation of the components present in the structure of clinoptilolite zeolite showed that the dominant component in the structure of this adsorbent is quartz, which constitutes 56% of the adsorbent structure. XRD analysis showed that the chemical composition of the zeolite is composed of oxides of silicon, potassium, sodium, iron, magnesium, calcium, and aluminum. The presence of these metal oxides causes the formation of functional groups on the surface of the zeolite when it is placed in water. These functional groups play an important role in the adsorption of pollutants from the liquid volume. By modifying the zeolite, its surface functional groups are changed, leading to an increase in its adsorption capacity.The modification of clinoptilolite zeolite with CTAB surfactant was found to significantly enhance its adsorption capacity for 2, 4-DNP from aqueous solutions. The presence of CTAB molecules on the zeolite surface introduced additional functional groups that interacted with the 2, 4-DNP molecules, leading to increased adsorption. The adsorption process was found to be pH-dependent, with the highest adsorption efficiency achieved at pH=7. The effect of temperature on adsorption was also investigated, and it was found that the removal efficiency decreased with decreasing temperature. The contact time between the adsorbent and the pollutant solution was also found to have a significant effect on adsorption, with increasing contact time leading to increased removal efficiency.

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