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Adsorption of chromium(VI) from an aqueous solution on a Syrian surfactant-modified zeolite

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Abstract: The adsorption of Cr(VI) from an aqueous solution on a Syrian surfactant-modified zeolite (SSMZ) was studied in a batch method. The SSMZ was prepared by adsorbing the cationic surfactant hexadecyltrimethyl ammonium bromide (HDTMA-Br) on the external surface of the zeolite. SSMZ was characterized by X-ray diffraction and Fourier transforms infrared analysis. The influence of pH solutions, initial concentration of Cr(VI), SSMZ dosage, surface coverage, granular dimensions and contact time were investigated. The experimental results showed that the highest removal efficiency occurs at pH1.5, Cr(VI) initial concentration of 15mg / L, SSMZ dosage of 5g / L, surface coverage of 200% of external cationic exchange capacity ECEC, granular dimensions of 75µm and contact time of about 7 hours. It must be mentioned that more than 85% of the Cr(VI) were removed within the first hour of the contact time. The results show that, SSMZ holds a great potential to remove Cr(VI) ions from solution. Key words: Syrian zeolite, chromate, Modification, Adsorption.

Introduction

Pure water progressively becomes a rare resource on earth, because of vast human activities that release increasing amounts of soluble and nonsoluble chemical species into natural water, that are not appropriately removed before returning water to the environment. Among the number of polluting species at issue are the ions of heavy metals [1]. Cr(VI) is known to be one of the heavy metal and is widely used in many industries including electroplating, leather tanning, dye, cement and photography industries. The effluents from these industries usually contain considerable amount of chromium, which ultimately spreads into the environment through soils and water streams and finally accumulates along the food chain which causes human health hazards [2]. The hexavalent form of chromium has been considered more hazardous to public health due to its mutagenic and carcinogenic properties [3-4]. The recommended limit of Cr(VI) in waste water is only 0.05 mg/L. But the industrial and mining effluents contain much higher concentrations compared to the permissible limit. Therefore, the concentrations of Cr(VI) must be reduced to levels that satisfy environmental regulations for various bodies of water [2].

Several treatment technologies have been developed to remove chromium from water and waste water. Common methods include chemical precipitation, ion exchange, membrane separation, elctrocoagulation, solvent extraction, sedimentation, reverse osmosis, dialysis, electrodialysis, cementation, air stripping, steam stripping, and flocculation [5-9]. However, these high-technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal [10].

Adsorption is versatile and effective method for removing Cr(VI). This, reduces the problem of sludge disposal and renders the system economically viable, especially when the adsorbents used are also of low cost. Adsorption process is used in a variety of important industrial applications and now it is increasingly used on large scale as an economical and efficient separation technique for metal ion removal from wastewater [11].

Use of various adsorbents such as bentonite [11], coal [12], and activated carbon [13] have been reported for the removal of heavy metals including Cr(VI) from aqueous solutions. Among the different minerals with adsorbent properties, zeolites are one of the most used adsorbents. The advantages of zeolites over resins are much lower cost. Zeolites have many applications such as molecular sieves and water softeners [14]. They appear also as suitable adsorbents for heavy metals; hence several investigations on adsorbent behavior of natural [15] and synthetic zeolites [16] is implemented.

Recently, interests on the adsorption of anions and neutral molecules by surface-modified zeolites is increased[17]. Zeolites in their original form could adsorb only cations, hence, development of materials with capability to adsorb anions, and neutral molecules is of high significance[18]. Zeolites could be treated using a cationic surfactant in order to do this. By treating, an organic layer is created on the external surfaces and the charge is reversed to positive [19]. Generally, HDTMA-Br is applied for zeolite treatment, which is a quaternary amine with a long chain cationic surfactant[20].

In this study, the possibility of using Syrian modified natural zeolite to remove Cr (VI) from aqueous solution is investigated. The effect of various parameters such as contact time, initial pH, surface coverage and initial concentration of Cr (VI) on the removal efficiency of zeolite was studied.

1. Experimental

1-1 Chemicals :

All used reagents were analytical grade and the solutions were prepared in deionised water. The stock solution of Cr (VI) with concentration of 1000 mg/L was prepared by dissolving 2.818 g of K₂Cr₂O₇ in 1000 mL deionised water in volumetric flask. Hydrochloric acid and/or sodium hydroxide solutions were used throughout experiments to adjust pH of the solution. 1, 5 diphenylcarbazide DPC was prepared by dissolving 0.25 gm of DPC in 100 ml of acetone, and stored in amber -colored bottle.

1-2 Analysis:

Chromium and HDTMA-Br concentrations were determined using UV-visible spectrophotometer model optizen 3220 UV, made in corea. Sodium concentration was determined using Flame Photometer, model BWB XP. The pH meter, model Martint made in Romania was used in this study .X-ray powder diffraction analysis was performed using XRD spectrometer model STOE Peak File(26462 pks) Cu K α radiation.

Determination of chemical composition of natural zeolite was performed using XRF model Seouential ARL 8410, made in germany. Fourier transform infrared spectroscopy of the zeolite has been studied using FTIR Analysis Instruments (Impact -415, made in united states). The spectra were recorded in the region 400-4000cm-1 with a spectral resolution of 2cm-1, using a pressed KBr pellet technique.

1-3 Sources of natural zeolite

The starting material for obtaining the surfactant modified zeolites was a natural Syrian zeolitic tuff taken from the Tel-Mkhelat deposit in south west of Syria. The zeolite crystals separated from rock sample were washed, dried, crushed and sieved to obtain fine powder, which dimensions ranging between75-600 µm. The powder was refluxed with doubly distilled water to remove soluble impurities. It was then decanted and dried in an oven for 24 hours. The fine powder of natural zeolite is used for further modification to enhance the activity. The chemical composition was determined by XRF technique. The results are presented in Table 1.

Table 1. The chemical composition of Zeonte									
SiO ₂ ,%	Al ₂ O ₃ ,%	CaO,%	MgO,%	Fe ₂ O ₃ ,%	K ₂ O,%	Na ₂ O,%	another comp,	L.O.I,%	
35.19	11.44	14.03	6.47	9.47	1.11	1.15	3.64	17.50	

Table 1. The chemical co	mposition of Zeolite
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The cation exchange capacity (CEC) of the zeolite was 1.31meq/g as determined by the 0.1 M NH₄OAc saturation method [21,22]. The external cation exchange capacity (ECEC) of the zeolite was determined to be 0.79 meq/g by the 1 mM (HDTMA- Br) saturation method[23].

1-4 Modification of Natural zeolite

Hexadecyltrimethylammonium (HDTMA-Br) was supplied by Merck-Schuchardt. Surfactant modified zeolite (SSMZ) was prepared by reacting zeolite (Na-form) with aqueous solutions of HDTMA-Br. HDTMA-

Br was added in an amount equal to either 50- 250 % of ECEC of the zeolite. This experiment was to study the effect of different surface coverage of HDTMA onto zeolite in the sorption of Cr(VI). The suspension was stirred for 3 days at 150 rpm on a shaker ,made in corea at 25°C. The mixture was then filtered by the vacuum filtration and the solid sample was dried at 60°C for overnight. The resultant SSMZ was characterized by X-ray powder diffraction (XRD) technique and FTIR Spectrophotometer in order to ensure that the structure of the zeolites did not collapse during the reaction with surfactant.

1-5 Chromate adsorption

Batch adsorption studies were carried out in 60 mL glass bottle with 25 mL of the working Cr(VI) solution of desired pH and concentration. The influence of pH(1.5, 2, 2.5, 3, 5, 7 and 10), initial Cr(VI) concentration (5-120 mgL⁻¹), contact time (1-24 hours), adsorbent dosage (0.1-0.5g), surface coverage (50-250% of ECEC) and granular diameters (75-600 μ m) were evaluated during the present study. At the end of the sorption period the supernatant was separated by centrifugation at 5000 rpm for 5 minute. Then the concentration of the residual Cr(VI) was determined by UV-visible spectrophotometer , using diphenyl carbazide [24,25] as the complexing agent. The amount of Cr(VI) (q) adsorbed in milligram per gram was determined by using the following mass balance equation:

$$q(mgg^{-1}) = \frac{(C_0 - C_f)V}{m}$$

Where C_0 and C_f are Cr(VI) concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in liter and m is the weight of the adsorbent in gram. The percentage of removal of Cr(VI) (R%) was calculated from the following equation:

3. Results and Discussion:

3.1. FTIR Spectroscopy:

The FTIR spectra of raw zeolite, HDTMA coated zeolite, Cr (VI) -adsorbed zeolite, and HDTMA-Br are presented in Fig. 1-3 respectively. The fact that zeolite are significantly hydrated is illustrated by the discrete water absorption bands centered at 3448 and 1637, refer to water molecules associated with Na and Ca in the channels and cages of the zeolite structure [21]. As can be seen from the fig.1, other bands appear at 1023 cm⁻¹ arise from asymmetric stretching vibration modes of internal T-O bonds in TO₄ tetrahedra (T=Si and Al). The 799 and 452 cm⁻¹ bands are assigned to the stretching vibration modes of O-T-O groups and the bending vibration modes of T-O bonds, respectively[26].

The HDTMA modified zeolites, in contrast to unmodified zeolites (fig.2.), have new bands at 2919 and 2850cm⁻¹, attributed to the antisymmetric (v_{as} CH₂) and symmetric (v_{s} CH₂) C-H stretching vibration modes of the methylene groups, respectively, testifies that the surface of the natural zeolite is covered by the alkylammonium bromides and/or alkylammonium cations [27]. the intensity of peak at 1431 cm⁻¹ attributed to vibration of trimethylammonium quaternary group CN(CH3)³⁺ [28]. Figure 2 shows that the adsorption of chromium on the surface of the modified natural zeolite weakens the intensity of peaks at 2850 and 2919cm⁻¹ suggesting that the active sites created by HDTMA were responsible for Cr (VI) removal from water[29]. This observation corroborated the fact that the Cr (VI) adsorption was of a physical nature, probably due to electrostatic forces between positively charged surfactant-modified zeolite and anionic Cr (VI).Finally most band positions did not change after modification and adsorption, suggesting that the basic zeolite structure did not collapse[20].



60 %T 40 20 4000 3000 1000 400

Figure1: The FTIR spectrum of raw zeolite



3.2. XRD Analysis:

The crystalline composite of Syrian zeolitic tuff based on internal standard X-ray diffraction analysis refer to be montimorilonite, phillipsite, calcite, and little percent of analcime.

By comparing the spectra of Na/ zeolite, Na/HDTMA-zeolite, (Fig. 4 and 5). we noticed some difference in the intensities of the peaks not in their locations Could be due to a mutual interaction between the internal surface of zeolite, and the surfactant [29]. we see also new peaks had been appeared on the spectrum after treatment with HDTMA-Br, We referred to it with red points (Fig 5).

Na/HDTMA-Cr-zeolite spectrum(Fig 6) shows decreasing in number of peaks in comparing with Na/HDTMA-zeolite spectrum, because the adsorption happened at strong acidic medium and the acid-treated clay minerals are known to give rise to an increase in the intensities of the very low angle diffraction bands[30]. so we see disappearing of some calcite peaks(We referred to it with red circle) and decrease intensity of another peaks implying a partial destruction of the structure compared to the parent clay[31].



Figure 6.XRD spectra of Na/HDTMA-Cr-zeolite

3.3 Cr (VI) adsorption Results:

3.3.1. Effect of Initial pH:

The removal of Cr (VI) from water by modified zeolite is highly dependent on the pH of the solution. The results are shown in Fig. 7. Maximum removal and adsorption capacity were found at pH 1.5. As the pH increased adsorption efficiency of Cr(VI) decreased .At pH 1.5, degree of surface protonation is high and so surface offers maximum positive charge for the adsorption of $HCrO_4^-$ anions which predominant at pH1.5. Therefore, at lower pH, it requires one exchange site from SSMZ for the $HCrO_4^-$ adsorption to occur, while at higher pH, it requires two exchange sites for one CrO_4^{-2} -species[20]. As the pH increased, the degree of surface protonation decreased and surface becomes more negative and then adsorption decreased [32,33]. Similar trend has been reported for the removal of Cr(VI) by activated carbon [34] and organo-modified zeolite [35].



Figure7: Effect of pH on Cr(VI) adsorption (Experimental conditions: Initial Cr(VI) concentration: 15 mg/L, adsorbent dose: 0.25 g/ 25 mL, agitation speed: 150 rpm, Temperature: 298.15 K, Contact time: 24h, percentage of surface coverage :200% of CEC, granular dimensions: 150 μm)

3.3.2.Effect of Cr(VI) concentration:

The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption. The effect of different initial Cr(VI) ion concentration on adsorption of Cr(VI) onto SSMZ presented in Fig. 8. As we can see from Fig.8, the adsorption capacity increased with increasing initial concentration of Cr(VI). It is possible that the initial concentration of the metal ions provides the necessary driving force to overcome the mass transfer resistance of Cr(VI) between the aqueous and the solid phase [36]. The increase in the initial Cr(VI) concentration also enhances the interaction between the Cr(VI) in the aqueous phase and the SSMZ surface. Similar results were obtained in the adsorption of Cr(VI) by natural plant material[37]. The percentage removal of Cr(VI), decreased with increasing of the initial Cr(VI) concentration. This can be explained by the fact that all adsorbents have a limited number of active sites and at a certain concentration the active sites become saturated[38].



Figure 8: Effect of Cr(VI) concentration (Experimental conditions: pH;1.5, adsorbent dose: 0.25 g/ 25 mL, agitation speed: 150 rpm, Temperature: 298.15 K, Contact time: 24h, percentage of surface coverage :200% of CEC, granular dimensions: 150 µm)

3.4.3. Effect of surface coverage:

Adsorption of Cr (VI) from a given solution was measured with different percentage of surface coverage of HDTMA-Br in the range of 50-250% of ECEC. The results are shown in Fig. 9. As we can see from Fig.9, the Cr(VI) removal and adsorption capacity increase with an increase in the percentage of coverage of the HDTMA and a value of 200% gives the best performance. Further increase in the percentage of coverage results in a decline in removal of Cr(VI). This may be due to the fact that the percentage of coverage > 200 % exceeds the surfactant critical micelle; which gives possibility to form a new layer that tends to weakens the attach between active sites on the surface of modified zeolite and Cr(VI).



Figure9: Effect of surface coverage (Experimental conditions: Initial Cr(VI) concentration: 15 mg/L, adsorbent dose: 0.25 g/ 25 mL, agitation speed: 150 rpm, Temperature: 298.15 K, Contact time: 24h, pH;1.5, granular dimensions: 150 µm)

3.3.4.Effect of adsorbent dosage:

The number of active sites relates to adsorbent dosage and hence adsorption performance. The effect of adsorbent dosage on the Cr(VI) percentage removal and adsorption capacity are shown in Fig. 10. It was found that the removal efficiency of Cr (VI) increased with increasing amount of the zeolite up to 0.25g. Further increase in the adsorbent dosage results in a small decline in removal of Cr(VI). This result was expected because for a fixed initial ion concentration, increasing adsorbent mass provides greater surface area and available adsorption sites [39]. However, it is observed that the increase in chromate percentage removal is not directly proportional to adsorbent mass . One plausible reason could be due the fact that, high adsorbent mass creates particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length [40].



Figure.10: Effect of adsorbent dosage (Experimental conditions: Initial Cr(VI) concentration: 15 mg/L, pH:1.5, agitation speed: 150 rpm, Temperature: 298.15 K, Contact time: 24h, percentage of surface coverage :200% of CEC, granular dimensions: 150 µm)

3.3.5.Effect of granular dimensions:

Adsorption of Cr (VI) from a given solution was measured with different granular dimensions in the range of 75μ m-600 μ m. Fig.11. shows variation of removal efficiency and adsorption capacity of Cr (VI) with granular dimensions. It was found that the removal efficiency and adsorption capacity of Cr (VI) increased with decreasing granular dimensions. This may be due to the fact that , decreasing granular dimensions of zeolite leads to increasing in zeolite surface and thus increasing in the degree of coverage with the surfactant which gives more number of active sites on the surface of the zeolite and then an increase in the removal efficiency.



Figure.11:Effect of granular dimensions(Experimental conditions: Initial Cr(VI) concentration: 15 mg/L, adsorbent dose: 0.25 g/ 25 mL, agitation speed: 150 rpm, Temperature: 298.15 K, Contact time: 24h, percentage of surface coverage :200% of CEC, pH:1.5)

3.3.6.Effect of contact time:

The removal efficiency also depends on contact time if other parameters like initial concentration, temperature, pH, etc. are kept constant. The effect of contact time on percentage removal and adsorption capacity of Cr (VI) is shown in Fig. 12. It shows that Cr (VI) removal increases with increasing contact time and approximately 80-85 % of maximum Cr(VI) removed is attained within the first hour and the maximum adsorption is attained in about 7-8 hours. No further increase in adsorption was noticed up to 24 h. The initial rapid rate of adsorption may be due to the availability of the positively charged surface of the adsorbent for anionic Cr (VI) species present in the solution. The later slow adsorption rate part of the curve may be due to the electrostatic hindrance caused by already adsorbed negatively charged adsorbate species and the slow pore diffusion of the ions[41].



Figure 12: Effect of contact time (Experimental conditions: Initial Cr(VI) concentration: 15 mg/L, adsorbent dose: 0.25 g/ 25 mL, agitation speed: 150 rpm, Temperature: 298.15 K, pH:1.5, percentage of surface coverage :200% of CEC, granular dimensions: 150 µm)

4. Conclusion:

In this work, adsorption of chromium ions from dilute solution with Syrian modified natural zeolite was investigated. The effect of several parameters such as pH solutions, initial concentration of Cr(VI), SSMZ dosage, surface coverage, granular dimensions and contact time, on the chromium adsorption was studied. According to experimental data, optimum operating condition for chromium adsorption with SSMZ were pH1.5, Cr(VI)initial concentration of 15mg / L, SSMZ dosage of 5g / L, surface coverage of 200% of ECEC, granular dimensions of 75 μ m and contact time of about 7 hours and under these condition nearly 95% of chromium ions was adsorbed by SSMZ. Maximum adsorption capacity of SSMZ was1.42 mg/g and this result shows that this SSMZ exhibits a reasonable capacity for chromium removal from aqueous solutions.

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