Research Article

Removal of Methylene Blue dye from Aqueous Solution by Modified Zeolite with Copper Oxide Nanoparticles

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ABSTRACT

Nanoparticles of sodalite zeolite were synthesized in this study then structure of zeolite was analyzed through XRF, XRD, SEM, and FTIR. Copper Nanoparticles (30-60 nm) have been used to modify the level of sodalite zeolite. The obtained results of analysis of scanning-spectroscopy Electron Microscope of Energy-dispersive X-ray (SEM-EDX) indicated the amount of copper on the zeolite level equal to 4/5 weight percent. To remove methylene blue dye from aqueous solution within batch process, acid treated zeolite (ATZ) and modified zeolite (MZ) with copper nanoparticles was used. The obtained results indicated that copper nanoparticles have a considerable effect on removal of methylene blue dye from aqueous solution. The maximum adsorption level was obtained to 97/2% (with amount of 6, 0/2g, and 20 min respectively for pH, absorbent dose, and contact time of MZ) and (6 amount, 0/3g, and 80min respectively for PH, adsorbent dose, and contact time of ATZ). Kinetic studies found that the methylene blue dye absorption process could be properly explained by pseudo-second-order kinetic model. In addition, Langmuir isotherm could properly cover equilibrium data with maximum absorption capacities of 61/72 and 15/11 mg/g respectively for MZ and ATZ. The results of tests indicated that increased temperature could negatively effect of removal efficiency. The thermodynamic parameters indicated that methylene blue dye absorption is exothermic and spontaneous within studied scientific conditions.

Keywords: nanoparticles, zeolite, copper, methylene blue, aqueous solution

1INTRODUCTION

The control of water pollution has become of increasing importance among governments and researchers through progress of industries in recent decade. The release of wastewater and pollutants such as dyes into the water cycle is an important issue increasingly considered in recent 20 years. Dyes are important part of many industries entering into water system and hard to remove. Many of industries such as paper, plastics, food, and textile use different types of dyes that textile industry has a more considerable role in use of industrial dyes among them. There are about 1000 types of industrial dyes causing severe environmental problems if they are not removed. Existence of dyes in minor amounts is also undesirable reducing water clearness and chemical reactions in water. Dyes are as hydrolyzed and solution in wastewater that are not removable by industrial filters. Some of dyes are resistant against removal methods due to their complex aromatic structure causing serious health problems even if they break into smaller particles, because they form inactive materials remaining as sludge
causing environmental problems [1]. Dye effluent should not be drained without adequate treatment due to toxic nature of dyes for many of plants and microorganisms. Even non-dye effluents prevent from light penetration resulting reduced photosynthetic yield of aquatic plants and increased COD [2]. Dye is the most unfavorable feature of textile effluents with harmful effects on environment. The growth of aquatic plants will stop due to light absorption by dye so that plants will disappear and this issue considerably affect water ecosystem. Among different removal methods, the removal methods of adsorption process have been considered more because of their efficiency and diversity. Zeolites are porous crystals at microscopic scale with extensive application for adsorption, catalyzing and ionic exchange. Sodalite is a mineral usually formed under laboratory conditions and hydrothermal synthesis belonged to zeolites. Sodalite is named after its sodium content. Sodalite has an aluminosilicate framework with an equal number of tetrahedral SiO4 and AlO4. Sodalite often is in the form of shaped phenocrysts with hexagonal cross. Sodalite has a pore size of 0/28nm [3]. Adsorption is a physical or chemical process in which, a material is accumulated and condensed at a joint surface of two phases. This phase can be liquid-liquid, gas-liquid, or liquid-solid. The material that is accumulated at one level is called adsorbate and the phase the material is absorbed on it is called adsorbent. There is a term against adsorption called as deep phenomenon in which, molecules or atoms of a phase are influencing into another phase to consist a uniform solution. The term of adsorption usually includes both types related to the process in which, one composition moves from one phase to accumulate in another phase especially if it is solid. Mc Bin [4] considered filter property of zeolites in 1932. He observed that zeolite chabasite would adsorb and hold vapor of relative small water molecules, formic acid and methyl alcohol but it does not adsorb larger molecules including acetone, ether, or benzene. Mc Bin found that selective adsorption is affected by dimensions of the pores of the crystals so that he noted the term of molecular sieve. This property of chabasite has been applied to prevent from entering of some pollutants such as sulfur dioxide gas through flues into atmosphere [5]. In general, adsorption mechanism is done through continuous steps: A- transmission dosage of molecules of adsorbate from solution dosage to the surface of solid particles, B- influence to internal structure of solid particles and placing in adsorption position, and C- rapid adsorption. The third step is so much rapid that no resistance is observed during sorption so that transmission dosage and inter-particle influence function as determining steps for adsorption speed; hence, transmission dosage is done through first minutes of process and influence of particle through several hours. Adsorption of materials on solid matter is caused by the gravity force between adsorbate and adsorbent surface. Removal of methylene blue dye was done by Qodaha et al in 2007 on an abundant mineral in Jordan called Acid treated diatomite (ATD) in order to improve its performance under the heat-treated with sulfuric acid. Equilibrium data were fitted with sorption isotherms of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich and Langmuir isotherms was more fitted with these data. Tests of sorption isotherms have been calculated with adding 0/1g of ATD to 100mg of methylene blue solution with 50mg/l concentration. Maximum adsorption capacity found 126/6 mg at 30EC. Pseudo-second-order kinetic model have better covered equilibrium data compared to pseudo-first-order kinetic and Morris model. The obtained results indicated that adsorption of methylene blue base dye on ATD is an endothermic and spontaneous process proved as an efficient adsorbent to adsorb alkaline dyes [6]. A study has been done by Hameed (2007) under the title of “Adsorption of methylene blue onto bamboo-based activated carbon”. Equilibrium data for adsorption of methylene blue with Langmuir isotherm indicated better fit compared to Freundlich isotherm and maximum adsorption capacity of monolayer found 452/2mg/g in initial concentration of 500mg/l and PH=7. Two kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption
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processes that the adsorption of methylene blue could be best described by the pseudo-second-order equation. In all experiments, 20mg of dyed solution of methylene blue with initial concentration of 100-500mg/l was taken and the dosage of added adsorbent found 0.2g at experiment temperature 30EC and required time of 48 hours to reach equilibrium [7]. On the other hand, another study has been conducted by Emad et al (2008) about removal of basic dyes such as methylene blue onto activated carbons. The aim of this study was to compare adsorption capacity of different types of activated carbons produced by steam activation in laboratory and industrial processes. Adsorption isotherm models of Freundlich, Langmuir and Redlich – Peterson have been applied for simulation of equilibrium data within different experimental parameters (PH and size of adsorbent particles) that the best fit was obtained using Redlich – Peterson isotherm with experimental data. In this study, It was found that PAC2 (activated carbon produced from New Zealand coal using steam activation) has the highest adsorptive capacity (about 230mg/l) towards MB dye (588 mg/g) followed by F400 (476 mg/g) and other activated carbons. The optimal calculated PH in these experiments found 11 at 20EC, adsorbent dose of 0.05g and dye volume of 50ml [8]. The purpose of present study is to synthesis of zeolite sodalite, modification of water level with copper nanoparticles and then application of modified zeolite to adsorb methylene blue. The effects of effective parameters such as PH, contact time, adsorbent dose, initial concentration and temperature in adsorption process have been assessed.

2Materials and methods
2.1- chemical materials
Properties of used chemicals in this study are described in table 1.

<table>
<thead>
<tr>
<th>Row</th>
<th>Chemical composition name</th>
<th>Company name</th>
<th>Purity percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methylene blue</td>
<td>Merck</td>
<td>99&lt;</td>
</tr>
<tr>
<td>2</td>
<td>Sodium meta-silicate</td>
<td>Fuka</td>
<td>99&lt;</td>
</tr>
<tr>
<td>3</td>
<td>Sodium aluminate</td>
<td>Merck</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>Sodium hydroxide</td>
<td>Merck</td>
<td>99&lt;</td>
</tr>
<tr>
<td>5</td>
<td>sulfuric acid</td>
<td>Merck</td>
<td>99&lt;</td>
</tr>
</tbody>
</table>

2.2- required equipment
The applied equipment is as follows:
- Scale model (BP 211D Sartorius)
- Magnetic stirrer model (Junke&Kunkle)
- Electric furnaces model (Binder FD-53)
- PH meter model (827 pH lab- Metrohm)
- Handmade polyethylene container (200mL)
- Teflon container coated steel (100 mL autoclave)
- Centrifuge machine model (DENLEY, BS400)
- Spectrophotometer device of UV-vis model (JENWAY 6320)
- X-ray diffraction (XRD) instrument model (Philips 1840, GBC AMM)
- Scanning electron microscope model (HITACHI, S-4160)
- Infrared spectrometer model (Perkin Elmer RXI)

2.3- Nanosodalite synthesis
In synthesis of nanosodalite, 1/837 g sodium aluminate was dissolved through mixing in 12mL sodium hydroxide 3/7M at 70°C and then the obtained homogeneous mixture was cooled to room temperature. 18/235 g of sodium meta-silicate was mixed and dissolved in 8mL sodium hydroxide 3/7M at 70°C and the cooled to room temperature. Aluminate solution was added to the silicate solution under vigorous stirring. Following, the obtained gel took time at room temperature for 1 hour under vigorous stirring before heating until reaching mixture of homogeneous gel. Then, gel transformed to steel autoclave and heated in oven at 100°C for 48h. Finally, the obtained sediments collected with filter paper treated twice with distilled water to reach to PH lower than 9 and then it was dried in oven at

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80°C. This zeolite was only used in continuous column.

2-3-1 Zeolite activation with acid
To activate zeolite, 5g zeolite sodalite in 100mL sulfuric acid 0/06M was under vigorous stirring at 87°C for 2h [9]. Acid-treated zeolite was treated several time with double-distillation distilled water and finally dried in oven at 110°C for 24h.

2-3-2- modification of zeolite sodalite with copper nanoparticles
0.1g of copper oxide nanoparticles (Cu2O) with size of 30-60nanometere was added to 10mL distilled water. The mixture was stirred for 30 min at 25°Cto obtain a homogenous mixture. Following, 2g zeolite sodalite was added to homogeneous mixture stirred for 2 hours at room temperature [10]. Finally, the mixture was dried in oven at 80°C for 10 hours.

2-3-3- determining properties of synthesized zeolite
To determine crystal structure and crystallinity degree of zeolite as well as phases in it, X-ray diffraction (XRD) was used. Morphology and surface structure of zeolite was determined using Scanning Electron Microscope (SEM). Before catching photos by SEM from sample, its surface was covered by gold using Sputter to improve its conductivity leading to catch more qualified photo. To identify factor groups, Fourier Transform Infrared technique was applied. To prepare sample, 1mg of adsorbent was uniformly combined with 100mg KBr and then the mixture was pressed on a transparent disc under the pressure of 200kgf/cm² for 5min. scanning domain for samples has been 600-4200 cm⁻¹.

2-4-Sorption experiments using synthesized zeolite
2-4-1- preparation of dye sample
To prepare suspension of methylene blue dye with different concentrations, first, a solution with 100mg concentration was prepared using a sample consistent of methylene blue dye with purity percentage of 96% was used and then different concentrations were diluted using this initial solution. 1-molar solutions of acid sulfuric (H2SO4 1M) and (NaOH 1M) were used to adjust the PH of solution in each experiment.

2-4-2- method of relevant experiments to batch sorption
Sorption experiments was non-continuously done using stirrer. Volume of all used solutions in these experiments considered equal to 100mL. After the end of each experiment, the solution and adsorbent were separated using centrifuge instrument and sample was prepared for analyze. PH of solution was adjusted by PH meter using solutions H2SO4 1M andNaOH 1M in each experiment. Each experiment was repeated twice at least to reduce error and the results were compared. Error level of experiments obtained lower than 4%. Adsorption efficiency of methylene blue dye within each experiment can be determined using equation (1):

\[
\text{Dye removal } \% = \frac{C_i - C_f}{C_i} \times 100
\]

In which, \(C_i\) (mg/L) is initial concentration and \(C_f\) (mg/L) final concentration of methylene blue dye. The equation (2) can be used to calculate the adsorbed level of methylene blue dye by adsorbent at t time:

\[
q_t = \frac{(C_i - C_f) \times V}{m}
\]

In which, \(q\) (mg/g) is equal to the adsorbed level of methylene blue dye per unit of adsorbent dosage in t time, \(C_i\) (mg/L) the concentration of methylene blue dye in aqueous solution in t time, \(V\) (L) volume of solution, and \(m\) (g) adsorbent mass. In addition, equation (3) can be used to calculate the amount of adsorbed methylene blue dye by adsorbent at equilibrium time:

\[
q_e = \frac{(C_i - C_f) \times V}{m}
\]

In which, \(q_e\) (mg/g) is the amount of adsorbed methylene blue dye per unit of adsorbent dosage at equilibrium time, and \(C_e\) (mg/L) the concentration of methylene blue dye in aqueous solution at equilibrium time.

2-4-3- determining optimal PH
It is essential to determine optimal PH in order to obtain optimal conditions of adsorption processes. To determine optimal PH within sorption of methylene blue dye by zeolite (modified zeolite with copper nanoparticles and acid-treated zeolite), 100mL solution of methylene blue dye with initial concentration of
50mg/l and 0/5g adsorbent were poured into 6 separated beakers. Different PHs at spectra of 3-8 were adjusted in each of beakers using PH meter instrument and solutions of 1M H₂SO₄ and NaOH and then each of beakers were placed on the stirrer with speed of 400rpm at room temperature for one hour. This part included examining the effect of initial PH on sorption process and there was not any action during experiment to keep PH stable. PH level was at first adjusted to considered amount and it was used in sorption process after adjustment of solution PH.

2-4-4- determining optimal contact time (equilibrium time)
To determine the optimal contact time, 0/5h adsorbent (modified zeolite with copper nanoparticles and acid-treated zeolite) was added to 100mL solution of methylene blue dye with initial concentration of 50mg/l and after adjustment of PH at optimal level obtained from previous step. Solution was placed onto the stirrer with speed of 400rpm at room temperature. Sampling was conducted within time intervals after beginning of sorption action. Solution and adsorbent in each sample was soon separated using centrifuge instrument and solution was prepared for analysis.

2-4-5- determining optimal adsorbent dosage
In these experiments also solutions of methylene blue dye with concentration of 50mg/l and volume of 100mL. Moreover, PH and contact time were adjusted for optimal level obtained from previous experiments. The selected amounts to study the effect of adsorbent dosage on removal efficiency and determine optimal adsorbent dosage in experiments of sorption of methylene blue dyes by acid-treated zeolite include amounts of 0/05 to 0/35 g and were equal to 0/05-0/3g for modified zeolite with copper nanoparticles. All of experiments conducted at room temperature, solution was separated from adsorbent by centrifuge after each sorption action, and solution was prepared for analysis.

2-4-6- examining method of effect of Initial Adequebit Concentration
The effect of initial adeorbit concentration on sorption process was examined for obtained optimal amounts of contact time, adsorbent dosage and, PH (for both adsorbents) from previous steps. The volume of solutions was also equal to 100mL in these experiments and sorption process was carried out at room temperature. To examine the effect of initial concentration of dye on removal efficiency, different concentrations of methylene blue dye were considered for both adsorbents (acid-treated zeolite and modified zeolite with copper nanoparticles).

2-4-7- examining method of temperature effect
Experiments were carried out at four temperatures 20, 30, 40, and 50°C with adding optimal adsorbent dosage to 100mL solution of methylene blue dye in order to determine optimal temperature within sorption process of methylene by zeolite. The other effective factors on experiment such as PH and contact time were all adjusted for obtained optimal amounts of previous steps. Water bath was used in these experiments to adjust the solution temperature in order to make a uniform temperature for solution. In each experiment, solution was separated from adsorbent by centrifuge after each sorption action, and solution was prepared for analysis.

2-4- Measurement of methylene blue dye concentration
Spectrophotometer device of UV-vies was used to measure concentration of methylene blue dye. For this purpose, maximum wavelength of dye (λmax) was measured first to measure the sorption of all samples at this wavelength. This wavelength for used dye was obtained to 664nm. Quartz cell (1cm) was used in all experiments.

3- DISCUSSION AND RESULTS
3-1- Evaluating chemical composition of zeolite by XRF
Chemical composition of zeolite sodalite is presented in table 2. As it is obvious, the main elements of zeolite sodalite include Si, O, Al, Na,Ca, and Fe as well as a few amounts of P, Mg, Mn, Ti, K, and S. it has been also reported in resources that zeolite sodalite have such
elements in their chemical composition. The applied zeolite sodalite in this research has 82/8 weight percentage of SiO₂, Al₂O₃, and Na₂O in accordance with indicated XRF analysis in table 2.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
</tr>
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<tbody>
<tr>
<td>Weight percent</td>
<td>40/01</td>
<td>28/81</td>
<td>24/01</td>
<td>0/11</td>
<td>0/02</td>
<td>0/02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Fe₃O₃</th>
<th>TiO₂</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>S</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percent</td>
<td>0/07</td>
<td>0/004</td>
<td>0/005</td>
<td>0/005</td>
<td>0/012</td>
<td>6/77</td>
</tr>
</tbody>
</table>

3.2 Evaluation of adsorbent structure by XRD

As it is depicted in this diagram, the prepared crystal sample by mentioned formulation is zeolite with sodalite type and its XRD results is based on standard XRD of this zeolite [11]. The obtained zeolite sodalite in 2θ values of 14/1°, 20/1°, 22/4°, 24/5°, 27/7°, 31/9°, 34/9°, 37/9°, 43/1°, 45/7°, and 48/1° have crystal peaks that these peaks are properties of zeolite sodalite presented by Tracy and Higgins [12].

3.2-2 XRD of zeolite after zeolite modification

Copper oxide nanoparticles (Cu₂O) with 30-60nm size were used to modify zeolite. Modified zeolite was also analyzed using XRD. According to the comparison between XRD model of modified zeolite and unmodified zeolite, it was determined that a peak had been appeared at 2θ =38/5° in after modification XRD indicating copper nanoparticles at surface of zeolite. On the other hand, intensity of sodalite peaks is reduced after process of ion exchange indicating replacement of copper ions with sodium ions [13].

XRD of zeolite sodalite before and after modification with copper nanoparticles is observed in diagram 2.

Diagram 2. XRD model of zeolite a) zeolite sodalite b) modified zeolite sodalite with copper nanoparticles
3.3- Morphologic evaluation of zeolite by SEM
The SEM image of zeolite sodalite prepared in this research is illustrated in diagram 3. As it is observed, the prepared zeolite in this study include particles with size of 30-50nm matched with the reference sample [14]. The modified zeolite sodalite has been analyzed through EDX-SEM to determine the amount of copper on the surface of zeolite. An EDX spectrum of modified zeolite has been illustrated in diagram 4. According to this diagram, it can be found that copper nanoparticles have been placed on the surface of zeolite. According to the result of EDX-SEM analysis, the amount of placed copper on zeolite surface is equal to 4/5 weight percentage (Table 3).

Diagram 3. SEM from zeolite a) prepared in this research b) reference [11]

Diagram 4. a) Relevant SEM image to modified zeolite with copper b) EDX spectra of modified zeolite

Table 3. Results of EDX-SEM for modified zeolite

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>49/13</td>
<td>O</td>
</tr>
<tr>
<td>17/07</td>
<td>Na</td>
</tr>
<tr>
<td>14/55</td>
<td>Al</td>
</tr>
<tr>
<td>14/75</td>
<td>Si</td>
</tr>
<tr>
<td>4/5</td>
<td>Cu</td>
</tr>
</tbody>
</table>

3.4- Evaluation of FTIR of zeolite sodalite
The FTIR image of synthesized zeolite is illustrated in diagram 5. Adsorption band at 3502 cm\(^{-1}\) can be attributed to structural hydroxyl groups (OH\(^{-}\)) of silicate network and the strongest vibration located at 991 cm\(^{-1}\) is
coordination four-dimensional Si in asymmetric tensile method [14 & 15]. In addition, peak at 707 cm\(^{-1}\) indicated bound of Al-O. Adsorption of 524 and 465 are respectively related to four-dimensional symmetric tensile method of Si\(_2\)O and bending method of existed T-O in units of TO\(_4\) (T=Si, Al). Emergence of peak of 435 cm\(^{-1}\) caused by formation of four-member loop of sodalite is one of the features to determine sodalite formation [14]. Tensile vibrations of T-O-T are observed at region of 670-730 cm\(^{-1}\). Since these vibrations are sensitive toward existed ion and action dosage in sodalite cage, the place of peak for encapsulated molecules such as H\(_2\)O and NaOH has high determining value [14 & 16]. One peak at region of 1648 cm\(^{-1}\) is related to the method of water variation.

**Diagram 5.** FTIR spectra of zeolite sodalite

3.5- Effect of initial PH of solution on removal efficiency

PH of solution is one of the most important factors of sorption process. PH is effective in process through three methods of absorbent surface charge, ionization degree, and changes in the nature of the adsorbate. The effect of PH on adsorption of methylene blue from aqueous solution by acid-treated zeolite sodalite (ATZ) and modified zeolite sodalite with copper (MZ) was assessed at PH range of 3-8 (diagram 6). Experiments were performed in initial concentration of 50 mg/l at temperature of 20°C. Moreover, amount of adsorbent in 100 mL solution of methylene blue dye has been equal to 0.5 g for ATZ and MZ. As it is shown in diagram, the action of methylene blue adsorption by both adsorbents is intensively related to PH level. With increase in PH to 6, the efficiency has been increased reaching to its maximum level while the efficiency of removal of methylene blue is reduced at PH≥7. It can be stated that increase in PH of aqueous solution would lead to increase in density of negative charge at the adsorbent surface. Therefore, adsorption of methylene blue can be attributed to the increase in negative charge on adsorbent surface (for instance zeolite). In addition, structures of zeolites are affected by acid so that bound of Si-O-Al is weaker than bound of Si-O-Si influenced by H\(^+\); in this case structure of zeolite is destroyed and this occurs for zeolites with low ratio of Si/Al (such as X, A, and Sodalite) [17]. Zeolites’ structures are severely affected by H\(^+\) ions at PHs<5; therefore, it would better for zeolites to have sorption action at PH>5 [18].
3-6 Effect of contact time on removal efficiency

The effect of contact time on sorption reaction of methylene blue on zeolites (ATZ and MZ) is illustrated in diagram 7. As it is obvious in this diagram, sorption efficiency will increase if the contact time is increased until the process is at equilibrium point with no further changes. It can be stated that at the beginning of reaction, the more increase in contact time duration, the more opportunity adsorbate particles have to influence on adsorbent and take active sites of adsorbent but when the process is balanced, adsorbent is saturated and increased contact time will have no effect on sorption efficiency. According to diagram 7, almost all amount of methylene blue dye has been removed by modified zeolite with copper (MZ) during 20min while only 28.5% of methylene blue dye was removed by ATZ during this time. As it is observed, more time is required to remove methylene blue dye and only 63% has been adsorbed after 80min. therefore, modification of zeolite with copper nanoparticles has a considerable effect on efficiency of removal of methylene blue dye by zeolite and large amount of dye has been removed by modified zeolite with copper during a short time.

Diagram 6. Effect of initial PH of efficiency of removal of methylene blue using ATZ and MZ

Diagram 7. Effect of contact time on efficiency of removal of methylene blue dye using ATZ and MZ
3-7- Effect of adsorbent dosage on removal efficiency
To examine the effect of adsorbent dosage on efficiency of removal of methylene blue dye by zeolite, different amounts of adsorbents of MZ and ATZ (0.05-0.35g) were treated in 100 mL aqueous solution of methylene blue dye with initial concentration of 50mg/l from methylene blue dye at optimal PH and contact time within separated experiments. The obtained results have been illustrated in diagram 8. As it is obvious, the removal efficiency is increased with increase in amount of zeolite. The results indicated that if there is an increase in amount of modified zeolite (MZ) equal to 0.2g and amount of acid-treated zeolite (ATZ) to 0.3g, there is no significant change in adsorption efficiency. Hence, 0.2g of MZ and 0.3g of ATZ were chosen as optimal amount of each of adsorbents and used in next experiments. The increase in sorption efficiency based on the increase in adsorbent dose can be justified in the way that with increase in adsorbent more places are prepared for a determined adsorbate; therefore, the increase in sorption efficiency is expected. However, after increase in a determined amount of adsorbent (MZ to 0.2g and ATZ to 0.3g) and because of fix amount of adsorbate (50mg/l) although there are more adsorbent places, but sorption level will not increase due to fixed composition of adsorbate (methylene blue dye).

![Diagram 8. Effect of adsorbent dosage on efficiency of removal of methylene blue dye onto MZ and ATZ](image)

3-8- Effect of initial concentration on sorption process
To examine the effect of initial concentration on sorption process, different concentrations of aqueous solution of methylene blue dye were prepared and sorption process performed within optimal conditions for adsorption process of methylene blue dye on MZ and ATZ (the range of initial concentration was chosen respectively equal to 50-120mg/l and 50-225mg/l for ATZ and MZ). The results can be observed in diagram 9. Accordingly, with increase in concentration of methylene blue dye in solution, the sorption efficiency has been decreased that this matter can be explained in the way that with increase in initial concentration, lack of enough active places for sorption in high concentration would lead to less adsorption. In other words, it can be stated that these places consist fixed amounts and they are occupied when the concentration increases; hence, sorption efficiency will decrease. On the other hand, the results indicate that only 34% of removal is done with increase in initial concentration of dye to 20mg/l by ATZ while removal efficiency for MZ is more than 53% with increase in concentration to 225mg/l that this matter indicates high positive effect of copper nanoparticles on removal of methylene blue dye.
3-9- Effect of temperature on removal efficiency

The effect of temperature degree on efficiency of removal of methylene blue dye from aqueous solution was assessed at four temperatures of 20, 30, 40, and 50°C by two types of zeolites (MZ and ATZ). Experiments were performed within the obtained optimal conditions from previous steps. The results are described in table 3. Accordingly, the increase in temperature in performed experiments by zeolite adsorbents have led to decrease in efficiency of removal of methylene blue dye from aqueous solution although this value has not been considerable. This matter can be explained in the way that with increase in temperature, thickness of border layer around the adsorbent is decreased; therefore, transmission of adsorbate from the solution to active sites of adsorbent will be harder leading to decrease in removal efficiency. On the other hand, increased temperature causes more molecule mobility so that the mutual effect between adsorbate and adsorbent will decrease resulting to reduced efficiency. Negative effect of temperature on removal efficiency indicates exothermic reaction of methylene blue dye adsorption [17 & 19].

3-10- Thermodynamic examination of process

Using existing data in table 4, thermodynamic of sorption processes has been discussed and parameters of changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been calculated based on equations (4), (5), and (6):

\[ K_c = \frac{F_2}{1 - F_2} \]

Table 4. Effect of temperature on efficiency of removal of methylene blue dye on MZ and ATZ

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Efficiency of ATZ removal (%)</th>
<th>Efficiency of ATZ removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>63/12</td>
<td>97/1</td>
</tr>
<tr>
<td>30</td>
<td>57/32</td>
<td>94/32</td>
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<td>550</td>
<td>50/2</td>
<td>78/23</td>
</tr>
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</table>
Removal of Methylene Blue dye from Aqueous Solution by Modified Zeolite with Copper Oxide Nanoparticles

In these equations, \( F_e \) is a fraction of methylene blue dye adsorbed at equilibrium mode. \( R(J/k.mol) \) is Universal Gas Constant and \( T(K) \) is absolute temperature.

Values of \( \Delta H \) and \( \Delta S \) can be obtained from slope and intercept of linear diagram of \( \log K_c \) based on \( 1/T \). Value of \( \Delta G \) are calculable at three temperatures using equation (4). The calculated thermodynamic parameters are presented in table (5). According to the results, enthalpy changes (\( \Delta H \)) are negative for both adsorbents indicating exothermic reaction of adsorption of methylene blue dye by both adsorbents. On the other hand, positive values of \( \Delta S \) for both processes indicate that joint level of solid and liquid phase is randomly increased at the time of stabilization of existing ions on the surface of adsorbent. Negative values of \( \Delta G \) at three temperatures indicating spontaneous reaction of methylene blue dye sorption from aqueous solution at four temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorbent material</th>
<th>( q_m ) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ATZ</td>
<td>15/43</td>
<td>Present study</td>
</tr>
<tr>
<td>2</td>
<td>MZ</td>
<td>61/73</td>
<td>Present study</td>
</tr>
<tr>
<td>3</td>
<td>Sawdust</td>
<td>19/41</td>
<td>[21]</td>
</tr>
<tr>
<td>4</td>
<td>PPy/SD</td>
<td>36/44</td>
<td>[21]</td>
</tr>
<tr>
<td>5</td>
<td>PAN/SD</td>
<td>3/8</td>
<td>[22]</td>
</tr>
<tr>
<td>6</td>
<td>Tea wastes</td>
<td>45/16</td>
<td>[23]</td>
</tr>
<tr>
<td>7</td>
<td>yellow passion fruit waste</td>
<td>44/7</td>
<td>[24]</td>
</tr>
<tr>
<td>8</td>
<td>Activated carbon</td>
<td>588</td>
<td>[8]</td>
</tr>
<tr>
<td>9</td>
<td>Pommel peel</td>
<td>344/83</td>
<td>[25]</td>
</tr>
</tbody>
</table>

3-11- Comparison of adsorbent with other adsorbents

To determine the ability of adsorbents MZ and ATZ to remove methylene blue dye, maximum sorption capacity of these adsorbents has been compared to other adsorbents in table 6. According to table 6, MZ adsorbent has higher sorption maximum than other adsorbents of ATZ, sawdust, PPy/SD, PAN/SD, tea wastes, and yellow passion fruit waste while MZ has a less sorption capacity compared to activated carbon with steam activation and Pommel peel. It can be concluded that prepared adsorbent in this research is appropriate to remove methylene blue dye from aqueous solution.
3-12- Revival of MZ zeolite

Revival of modified zeolite with copper is vitally important to remove adsorbed methylene blue dye on the copper to reuse it within industrial operations. Relevant experiments to adsorbent revival were carried out using oven at 550°C to decompose the dye. To indicate capability of reapplication of adsorbent, sorption and removal cycles of methylene blue dye treated for five times.

According to the obtained results of table 7, removal efficiency has not considerable changed within sorption and removal processes and reduction of removal efficiency has been less than 6%. Therefore, reuse of adsorbent is an important feature to apply it in continuous systems within industrial processes.

Table 7. Revival of modified zeolite with copper to remove adsorbed methylene blue dye

<table>
<thead>
<tr>
<th>Step</th>
<th>Efficiency of removal of methylene blue dye (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step one</td>
<td>97/8</td>
</tr>
<tr>
<td>Step two</td>
<td>96/89</td>
</tr>
<tr>
<td>Step three</td>
<td>94/66</td>
</tr>
<tr>
<td>Step four</td>
<td>93/16</td>
</tr>
<tr>
<td>Step five</td>
<td>91/88</td>
</tr>
</tbody>
</table>

4- CONCLUSION AND SUGGESTIONS

At first, features of Nano zeolite sodalite were prepared and assessed using XRD, SEM, and FTIR techniques. Relevant experiments to removal of methylene blue dye from aqueous solution within batch system by two adsorbents of acid-treated zeolite sodalite and modified zeolite with copper nanoparticles.

The optimal PH was obtained to 6 for both adsorbents. Almost all of the methylene blue dye (98%) was removed by modified zeolite with copper (MZ) during 20min and this time reported as the optimal time for this adsorbent while it was observed that acid treated zeolite (ATZ) needs more time to remove methylene blue dye and only 63% was adsorbed after 80min. The relevant results to adsorbent dosage indicated that with increase in amount of zeolite from 0/05 to 0/2 and 0/3g respectively for MZ and ATZ, removal efficiency increased but there was not any change after that. Hence, 0/2g of MZ and 0/3g of ATZ were chosen as optimal dose for each adsorbent and this optimal dosage was used in next experiments.

To examine the effect of initial concentration of methylene blue dye on removal efficiency on adsorbent, the initial concentration ranges of 50-120mg/l and 150-225mg/l were respectively chosen for ATZ and MZ. The relevant experiments were conducted in 100mL aqueous solution of methylene blue dye. Thermodynamic assessment of these processes indicated negative Gibbs energy and spontaneous reaction as well as exothermic reaction because of negative enthalpy.

REFERENCES

equilibrium study, Desalination and Water Treatment, 57 (2016) 1880-1889.


