

Preparation and evaluation of alginate nanocomposite containing clay and zein to remove tartrazine dye from aqueous solution

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Abstract:

The use of clay-based nanocomposites as bioadsorbents was considered in this research due to their high mechanical and chemical stable properties, cheapness, compatibility, and abundance in nature. Thermal solution method was used to produce montmorillonite-alginate-zein (MMTALgZ) nanocomposites to remove tartazine dye. Zein and alginate polymers were used to modify the surface of clay. The samples were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX), and ultraviolet-visible (UV-Vis) spectroscopy. The effects of temperature, amount of nanoadsorbent, and contact time on the removal efficiency were investigated. Based on the results, increasing the time (180 min), decreasing the amount of sample (0.1 g) and increasing the temperature (90 °C) increased the absorption of nanocomposite. Also, the nanocomposite is used as a bioadsorbent for the decolorization of tartrazine as azo dye. For the optimal sample, more than 97% of the tartrazine dye was adsorbed by the MMT ALgZ nanocomposite was done in a much shorter time. Hence, nanocomposite-based nanobiosorbent can be a good candidate for adsorption and decolorization of various azo dyes.

Keywords: Alginate; Clay; Nanocomposite; Tartrazine; Zein

1. Introduction

Toxic dyes are known as one of the main pollutants with harmful effects on the environment and living organisms [1]. In chemistry, compounds with the molecular form R-N=N-R are called azo, the group N=N is the functional group of azo. Liquid composition containing pigments and azo dyes that have substituents such as sulfonic acid groups are widely used [2]. Tartrazine is a synthetic lemon yellow or orange azo dye with a pH constant of approximately 3 to 8 with stability to light, heat, and environments. Disadvantages of this dye are its undesirable release in water, the potential of mutagenesis and carcinogenesis in people, and

the production of toxic by-products in aquatic environments was the most important reason. In addition, the entry of wastewater with this dye causes an ecological effect and the phenomenon of eutrophication [3]. Physical, chemical and biological methods have been developed to remove dyes [4]. Among these methods, adsorption technology is a competitive dye removal method due to its high efficiency, economic feasibility, and design simplicity [5]. The main mechanisms of dye removal by adsorption are electrostatic attraction, ion exchange, surface complexation and $\pi-\pi$ interactions [6]. Composites as adsorbents can play an effective role in improving absorption [7]. Environmentally friendly nanocomposites have been developed for the treat-

ment of dye effluents due to their potential [8]. Sodium alginate (SA) is a natural hydrophilic polysaccharide with low toxicity, good biocompatibility and biodegradability [9]. Alginate has been of interest in recent years due to its unique properties [10]. One of the important applications of alginate biopolymer is the removal of heavy metals [11] and dye [12, 13] from wastewater. Zein (ZN) is a natural biocompatible and hydrophobic corn-derived protein with major benefits [14]. The application of zein has expanded due to its potential [15, 16]. Adsorbents are one of the important applications of zein biopolymer [17, 18]. Clay, which is a natural material, is widely used due to its special properties [19]. These distinctive properties have led to the widespread use of clay-based adsorbents for dye removal [20, 21]. So far, there have been reports for hexavalent chromium adsorption by montmorillonite-supported magnetite nanoparticles [22] (montmorillonite was chosen accordingly), two azo anionic textile dyes including Direct Blue 78 and Direct Yellow 106 by alginate-chitosan beads [23] (alginate was chosen accordingly), cinnamon essential oil adsorption by bio-based zein containing chitosan nanoparticles [24] (zein was chosen accordingly) and Rhodamine 6G absorption by chitosan–clay nanocomposite [25] (montmorillonite was chosen accordingly) is presented for the water treatment process. Therefore, the novelty, innovation, objective and significance of this research was to use bio-inspired compounds with a simple, fast and cheap method to investigate the simultaneous presence and synergistic effect of alginate, clay and zein in MMTALgZ nanocomposites to remove tartazine dye from aqueous solution as a low-cost, convenient and fast azo dye biosorbent to solve the challenge of water pollution.

2. Experimental

2.1 Materials

All chemicals including tartrazine dye, sodium alginate, zein, montmorillonite, and ethanol were obtained from Sigma-Aldrich.

2.2 Preparation of samples

Modified montmorillonite was prepared by adding 8 g of MMT to 50 cc of 20% (V/V) hydroalcoholic solvent under stirring and sonication. Alginate 2% (W/V) was prepared by adding 2 g of sodium alginate to 100 cc water solvent. Zein 2% (W/V) was prepared by adding 2 g of zein to 85 cc hydroalcoholic and 15 cc water solvent.

Alginate-montmorillonite nanocomposite was prepared by adding 50 cc of 2% (W/V) sodium alginate solution and slowly added to modified montmorillonite solution and stirred for 2 h. Finally, the sample was separated and dried for 24 h.

Zein-montmorillonite nanocomposite was prepared by adding 50 cc of 2% (W/V) zein solution and slowly added to modified montmorillonite solution and stirred for 2 h. Finally, the sample was separated and dried for 24 h.

Alginate-zein-montmorillonite nanocomposite was prepared by adding 50 cc of 2% (W/V) zein solution and slowly added to 50 cc of 2% (W/V) sodium alginate solution and stirred for 2 h. Then the solution was slowly added to 50 cc

of modified montmorillonite and stirred for 2 h. Finally, the sample was separated and dried for 24 h.

Tartrazine solution was prepared in water solvent with an initial concentration of 50 ppm. Then it was prepared by diluting other concentrations.

2.3 Characterization techniques

FTIR was performed on potassium bromide (KBr) disc method via Perkin Elmer spectrometer (England) for the investigation of functional groups. XRD was obtained using Panalytical X'pert diffractometer (Netherlands) at room temperature under Cu K α irradiation ($\lambda = 0.15406$ nm) for evaluation of crystal structure. FESEM and EDX were evaluated by ZEISS (Germany) for observation of size, morphology, and chemical composition. Tartrazine adsorption was measured by UV–Vis spectroscopy at the max wavelength of 424 nm (GENESYS 30 model, Thermo Scientific, America).

3. Results and discussion

3.1 FTIR

FTIR spectra of samples were recorded in the range of 400 – 4000 cm $^{-1}$ (Fig. 1). For montmorillonite (Fig. 1a), the absorption band in the region of 3446.03 cm $^{-1}$ is attributed to the hydroxyl group (O-H) present in the sample. In addition, the absorption bands corresponding to the bending vibrations of the hydroxyl group in water molecules adsorbed on the surface of montmorillonite were observed at 1634.97 cm $^{-1}$. Also, the sharp and strong absorption peak at 1047.88 cm $^{-1}$ is related to the out-of-plane stretching vibration of the Si-O bond in the structure of the montmorillonite. Absorption lights related to vibrations of aliphatic hydrocarbon -CH $_2$ appeared at 2826.59 cm $^{-1}$. The two absorption bands observed in the range of 459 and 793 cm $^{-1}$ are related to the bending vibrations of Si-O and AlAOH, respectively [26].

For alginate (Fig. 1b), the broad absorption band that appears at 3000 – 3433 cm $^{-1}$ is related to the stretching vibrations of the hydroxyl functional group. Other absorption bands in the regions of 2409.72 and 2925.8 cm $^{-1}$ are attributed to aliphatic C-H stretching vibrations. In addition, the absorption bands observed in the regions of 1617.86 and 1370.77 cm $^{-1}$ are attributed to the symmetric and asymmetric stretching vibrations of the carboxylate salt ion (COO $^-$) in the alginate structure. Also, the absorption bands related to stretching vibrations (C-O) in the first type of alcohol groups were observed at 1015.43 cm $^{-1}$ [27].

For zein (Fig. 1c), the broad absorption band that appears at 3432 cm $^{-1}$ is related to the OH functional group. Two absorption bands in the range of 1641.59 and 1426 cm $^{-1}$ are attributed to the stretching vibrations of C=O and C-N functional groups, respectively [28].

For montmorillonite-alginate nanocomposite (Fig. 1d), the synergy of the absorption band related to the OH functional group is in the range of 3000 – 3434 cm $^{-1}$ has widened its intensity is also increased compared to pure montmorillonite [29]. In addition, the addition of montmorillonite to alginate caused the absorption band corresponding to the COO $^-$ group to shift from 1617.87 to 1625.21 cm $^{-1}$. Also,

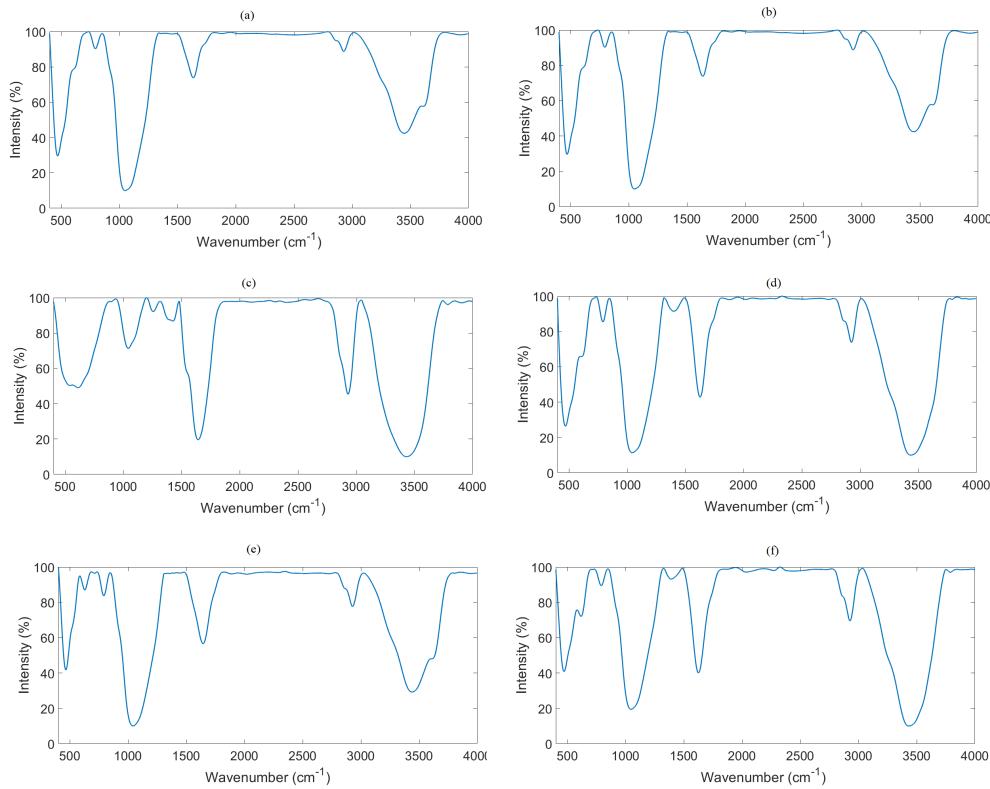


Figure 1. FTIR spectra of a) montmorillonite, b) alginate, c) zein, d) montmorillonite-alginate nanocomposite, e) montmorillonite-zein nanocomposite, f) montmorillonite-alginate-zein nanocomposite.

the absorption bands related to the chemical structure of the montmorillonite were observed in the range of 486.47, 790.88 and 1041.91 cm^{-1} . The absorption band at 1398.7 cm^{-1} is related to the stretching vibration of C-O bonds of alcoholic groups and C-O-C of ether groups in the alginate structure, which can be correctly confirmed as a result of the formation of montmorillonite-alginate nanocomposite. For montmorillonite-zinc nanocomposite (Figure 1e), by comparing the FTIR spectra of montmorillonite and zinc samples, the characteristic peaks of each can be clearly observed, with the difference that a slight change in their absorption frequency occurred after hydrogen interaction and modification the surface of the clay substrate. The frequency of the absorption band corresponding to the C-O stretching vibrations of the first type amide (I) has changed from 1642 to 1624 cm^{-1} . This displacement occurred due to the interaction of protonated amino groups with negatively charged sites in the structure of montmorillonite [30]. Similar results regarding the changes in amide I bond in zein have been reported by other researchers. In addition, the change in the stretching vibrations of the N-H group also occurred and shifted to higher wave numbers. These observations indicate the existence of hydrogen bonding interactions between amide groups in zein and surface water molecules in montmorillonite.

For montmorillonite-alginate-zein nanocomposite (Figure 1f), it is clear that all the absorption peaks corresponding to all three compounds can be observed in the obtained FTIR spectrum with a slight shift due to the interaction

between the components. The shift of the absorption band located at 1643 cm^{-1} and the decrease in the intensity of the corresponding peak indicate the hydrogen interaction between alginate and zein and the surface modification of the nanocomposite based on montmorillonite [31].

3.2 XRD

The XRD patterns of samples were evaluated in 2θ range $5 - 80^\circ$ (Fig. 2). For montmorillonite (Fig 2a), the main characteristic diffraction peak was observed at $2\theta = 7.1^\circ$, which corresponds to the (001) plane. The XRD pattern of montmorillonite confirmed the previous report [32]. For alginate (Fig 2b), the two characteristic peaks were shown at $2\theta = 19.1$ and 34.2° , corresponding to (111) and (200) planes, respectively. The XRD pattern of alginate confirmed the previous report [33]. For zein (Fig 2c), the two main characteristic peaks at $2\theta = 9.5$ and 20.3° are attributed to the entanglement or alpha-helix and β -sheet in the zein protein network. The XRD pattern of zein confirmed the previous report [34]. For montmorillonite-alginate nanocomposite (Fig 2d), the characteristic diffraction peak intensity of montmorillonite at $2\theta = 1.7^\circ$ decreases slightly after adding alginate, but in general its crystal structure is maintained in the nanocomposite. In addition, the intensity of the diffraction peak related to the alginate polymer also decreased after being composited with montmorillonite and slightly shifted to smaller angles. For montmorillonite-zein nanocomposite (Fig 2e), the intensity of the characteristic diffraction peaks of montmorillonite and zein at $2\theta = 7.09$ and 19.82°

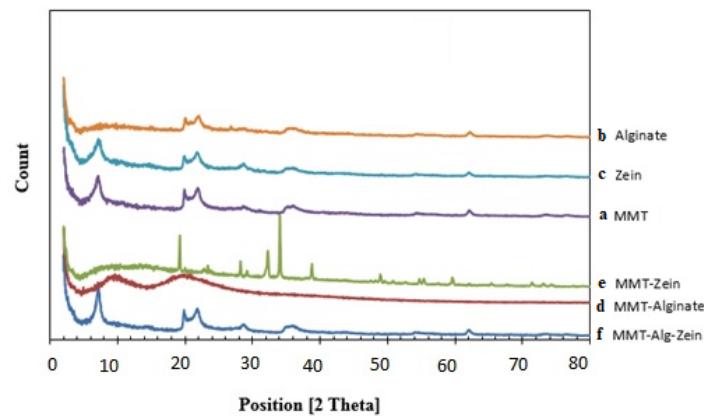


Figure 2. XRD spectra of a) montmorillonite, b) alginate, c) zein, d) montmorillonite-alginate nanocomposite, e) montmorillonite-zein nanocomposite, f) montmorillonite-alginate-zein nanocomposite.

decreased after the formation of the composite. As a result, the structure and crystal phase of montmorillonite are preserved in the montmorillonite-zein nanocomposite. For montmorillonite-alginate-zein nanocomposite (Fig 2f), the octahedral crystal structure of montmorillonite according to the diffraction standard 99 – 002 – 0037 was preserved in the final nanocomposite and the intensity of the characteristic peaks decreased after the formation of the composite with zein and alginate as expected. The appearance of new peaks at $2\theta = 20 - 30^\circ$ indicates the surface modification of clay by zein and alginate biopolymers.

Based on the comparison between the XRD patterns of samples obtained in the present research, it can be seen that the structure and crystal phase of montmorillonite did not change much after the addition of alginate and zein and still kept its crystal structure. Also, the intensity of the peaks related to the crystalline structure of zein and alginate at $2\theta = 20 - 30^\circ$ has decreased after being composited with clay, which indicates the successful formation of the nanocomposite.

3.3 FESEM

FESEM images of the samples are shown in Figure 3. Based on the results, the montmorillonite clay has a layered, heterogeneous, dense and compact structure with the thickness of the layers from 35 nm (Fig. 3a). The results confirm the previous report [35].

FESEM image of montmorillonite-alginate nanocomposite shows that the layered structure of MMT nano clay is well preserved and agglomeration occurs after the addition of alginate biopolymer (Fig. 3b). Also, the presence of alginate particles on MMT surface is clearly visible. The average thickness of the layers is about 35 nm.

FESEM image of montmorillonite-zein nanocomposite shows that the approximate average diameter of the layers is about 35 nm (Fig. 3c). Based on the results, montmorillonite maintains its sheet and layer structure and the surface coating by zein protein is clearly seen. Also, the amount of aggregation increased slightly after the addition of zein. Based on FESEM results of montmorillonite-zein-alginate nanocomposite, the final nanocomposite has a layered and dense structure (Fig. 3d). After adding zein and alginate

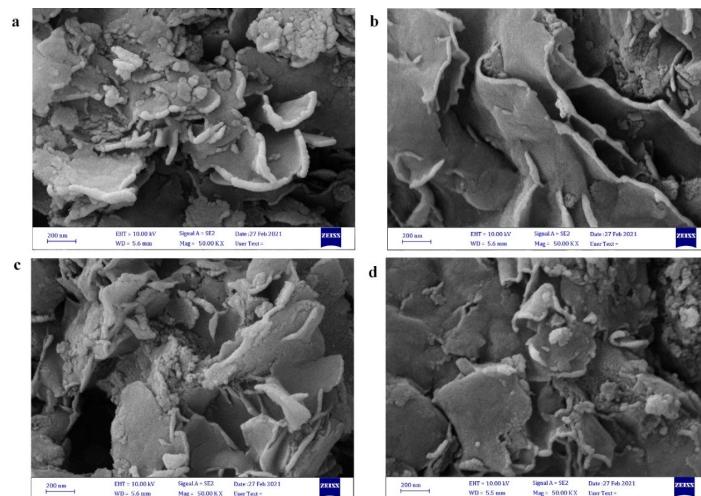


Figure 3. FESEM of a) montmorillonite, b) montmorillonite-alginate nanocomposite, c) montmorillonite-zein nanocomposite, d) montmorillonite-alginate-zein nanocomposite.

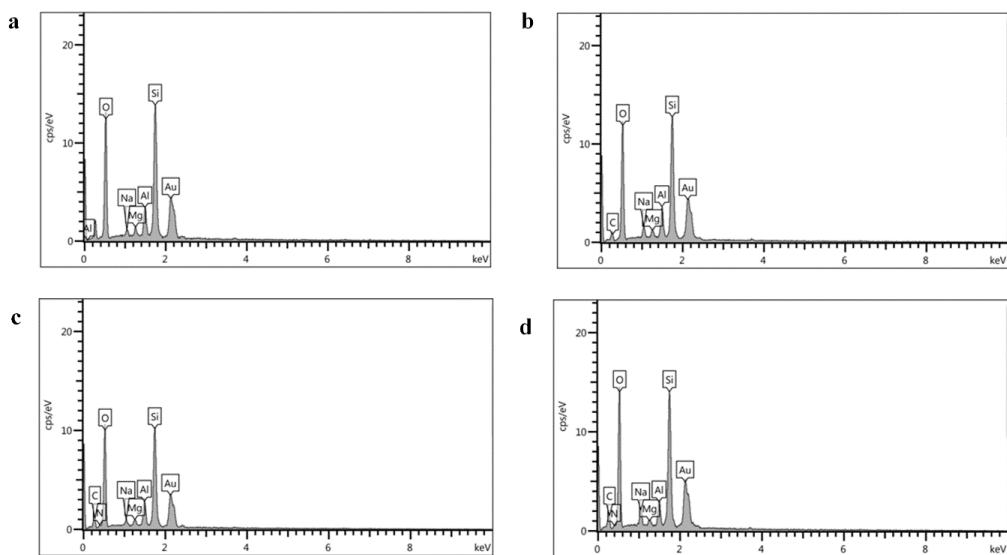


Figure 4. EDX of a) montmorillonite, b) montmorillonite-alginate nanocomposite, c) montmorillonite-zein nanocomposite, d) montmorilonite-alginate-zein nanocomposite.

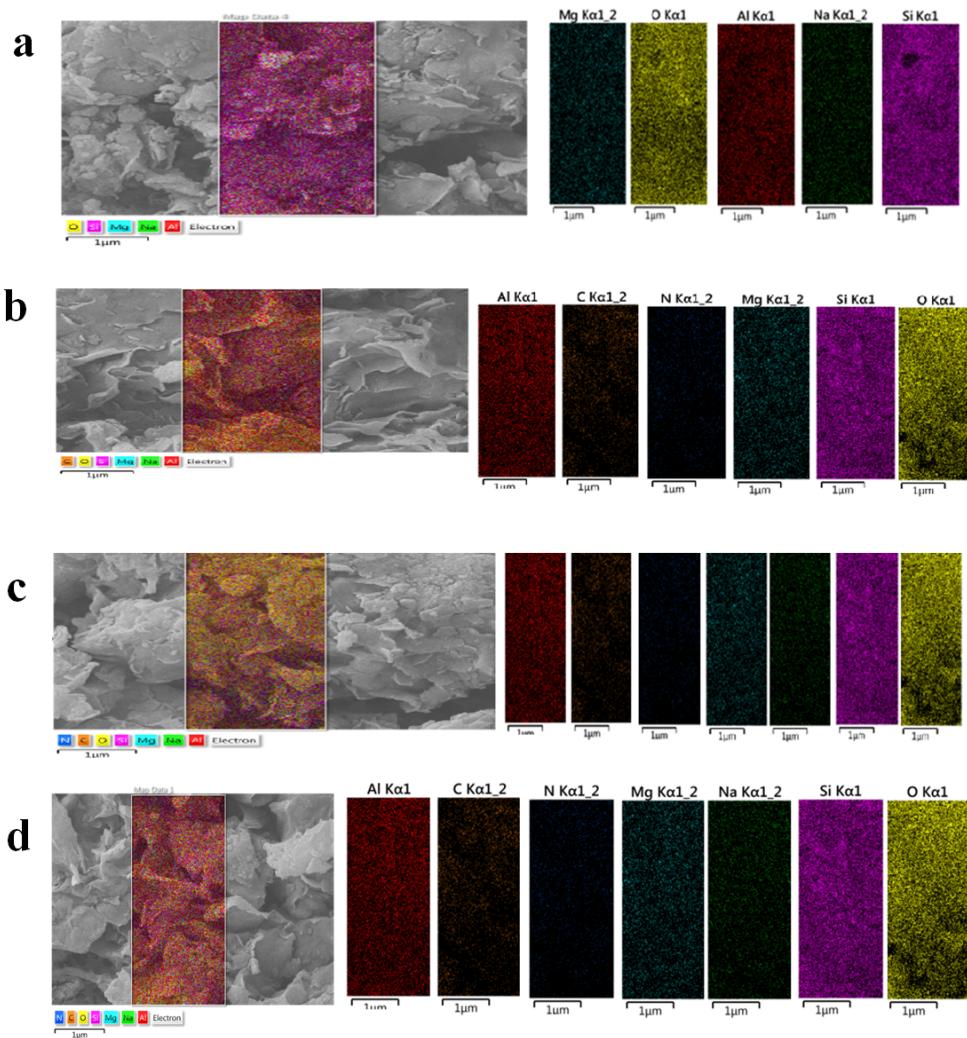


Figure 5. EDX of a) montmorillonite, b) montmorillonite-alginate nanocomposite, c) montmorillonite-zein nanocomposite, d) montmorilonite-alginate-zein nanocomposite.

Table 1. Effects of contact time on tartrazine dye absorption.

| Samples | Dye absorption (%) | Time (min) |
|---|--------------------|------------|
| Montmorillonite-alginate-zein nanocomposite | 58.41 | 30 |
| | 66.11 | 60 |
| | 81.03 | 120 |
| | 93.13 | 180 |
| Montmorillonite-zein nanocomposite | 61.2 | 180 |
| Montmorillonite-alginate nanocomposite | 54.45 | 180 |
| Alginate | 54.33 | 180 |
| Zein | 62.76 | 180 |
| Montmorillonite | 60.32 | 180 |

biopolymer, the amount of accumulation and density of the layers increased slightly. Also, the presence of polymer on the surface of clay is quite evident. The thickness of the layers has also increased and the approximate diameter of the layers is about 35 nm.

3.4 EDX and mapping analysis

EDX images of the samples are shown in Figure 4. The gold element visible in the EDX spectrum was used to conduct the sample. For montmorillonite, the chemical structure consists of oxygen, magnesium, aluminum, sodium and silicon. The EDX result of montmorillonite confirmed the previous report [36]. For montmorillonite-alginate nanocomposite, the chemical structure of the sample consists of Si, O, Al, Mg, Na and C elements. The presence of carbon in the chemical structure of montmorillonite-alginate nanocomposite indicates surface modification by alginate biopolymer [37]. As a result, the successful preparation of montmorillonite-alginate nanocomposite was confirmed. For montmorillonite-zein nanocomposite, in addition to the elements of the chemical structure of montmorillonite, the presence of carbon and nitrogen elements indicates its surface modification with zein protein [38, 39]. As a result, the successful preparation of montmorillonite-zein nanocomposite was confirmed. For montmorillonite-zein-

alginate nanocomposite, the amount of carbon increased significantly after the simultaneous addition of zein and alginate biopolymers. Also, the presence of nitrogen element confirms the surface modification of clay nanoparticles by zein polymer. According to the results, it is possible to report the successful preparation of montmorillonite-zinc-alginate nanocomposite.

The mapping analysis images of the samples are shown in Figure 5. This analysis confirmed the chemical structure and uniform elemental distribution.

3.5 Adsorption

The tartrazine adsorption was investigated by calibration curve using UV–Vis spectroscopy at $\lambda_{max} = 424$ nm. The goal is to achieve high absorption with low amounts of biosorbent by checking the effect of time, nanoadsorbent amount, and temperature. The results based are presented based on the removal percentage provided and the formula is as follows:

$$\text{Removal\%} = \frac{(A_0 - A_t)}{A_0} \times 100$$

where A_0 is the initial adsorbent and A_t is the adsorbent of the azo dye solution at time t . 0.1 g of adsorbent was placed in the vicinity of 2 ml of tartrazine dye with a concentration

Table 2. Effects of nanoadsorbent amount on absorption of tartrazine dye.

| Samples | Dye absorption (%) | Nanoadsorbent amount(g) |
|---|--------------------|-------------------------|
| Montmorillonite-alginate-zein nanocomposite | 92.32 | 0.05 |
| | 93.25 | 0.2 |
| Montmorillonite-zein nanocomposite | 47.76 | 0.05 |
| | 85.45 | 0.2 |
| Montmorillonite-alginate nanocomposite | 54.39 | 0.05 |
| | 89.76 | 0.2 |
| Alginate | 53.46 | 0.05 |
| | 58.24 | 0.2 |
| Zein | 57.53 | 0.05 |
| | 87.78 | 0.2 |
| Montmorillonite | 49.68 | 0.05 |
| | 85.80 | 0.2 |

Table 3. Effects of temperature on the amount of absorption of tartrazine dye.

| Samples | Dye absorption (%) | Temperature (°C) |
|---|--------------------|------------------|
| Montmorillonite-alginate-zein nanocomposite | 97.26 | 50 |
| | 97.67 | 70 |
| | 99.36 | 90 |
| Montmorillonite-zein nanocomposite | 86.03 | 50 |
| | 88.36 | 70 |
| | 90.69 | 90 |
| Montmorillonite-alginate nanocomposite | 72.36 | 50 |
| | 81.50 | 70 |
| | 81.01 | 90 |
| Alginate | 61.37 | 50 |
| | 71.43 | 70 |
| | 72.36 | 90 |
| Zein | 66.84 | 50 |
| | 68.58 | 70 |
| | 84.87 | 90 |
| Montmorillonite | 68.52 | 50 |
| | 69.57 | 70 |
| | 72.48 | 90 |

of 5 ppm at different times and the amount of adsorption was checked.

3.5.1 The effect of time

The contact time between the nanoadsorbent and the adsorbed pollutant is one of the most effective and important factors in the investigation of dye removal. For this purpose, the effect of 30, 60, 120, and 180 min on the removal of tartazine dye by 0.1 g of montmorillonite-alginate-zinc nanocomposite was investigated (Table 1). Based on the results, 180 min showed the best efficiency (93.13) for the montmorillonite-alginate-zinc nanocomposite, and as a result, it was chosen as the optimal time for subsequent analyses. In the optimal final composition based on the preparation method, the amount of montmorillonite, alginate, and zein are 16% (W/V), 2% (W/V), and 2% (W/V) respectively.

3.5.2 The effect of nanoadsorbent amount

0.1, 0.2, and 0.05 g of samples were placed in the vicinity of tartrazine dye solution with a concentration of 5 ppm for 180 min (Table 2). Based on the results, more nanoadsorbent can adsorb more amount of tartrazine dye pollutant due to increased surface area. As a result, 0.05 g of the montmorillonite-alginate-zinc nanocomposite was selected as the optimal amount of nanoadsorbent. The highest removal efficiency (93%) was obtained using 0.2 g of this nanocomposite. By comparing the results of the similar absorption percentage of two samples of 0.1 and 0.2 g, therefore, the sample with a lower amount (0.1 g) is preferable.

3.5.3 The effect of temperature

Considering that the nanocomposite was tested at laboratory temperature, the effect of different temperatures including

50, 70 and 90°C on the removal of tartrazine dye was investigated (Table 3). 0.1 g of sample was exposed to tartrazine pollutant. Based on the results, in general, the increase in temperature causes an increase in absorption due to an increase in the movement of dissolved particles. In this research the factors of time, nanoadsorbent amount and temperature on absorption efficiency were investigated and factors such as pH, particle size, concentration, reproducibility, etc. can be investigated in future reports to find a low-cost nanoadsorbent for review of kinetic and isotherm studies.

4. Conclusion

In this research, alginate-montmorillonite-zinc nanocomposite adsorbed and destroyed tartrazine dye from aqueous solution with an efficiency higher than 90%. The sample was characterized using FTIR, XRD, FESEM, EDX, and UV-Vis spectroscopy. According to the results, the nanocomposite was suggested as an economic source and good candidates for tartrazine absorption. But there is a possibility of limiting production on an industrial scale. In general, the dye absorption increased with increasing time, nanoadsorbent amount, and temperature. The expansion of the application of wastewater decolorization by this nanocomposite is important due to its advantages such as low cost of materials, ease of preparation, and biocompatibility, and it can develop the future perspective.

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Ethical approval

This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval is not applicable.

Authors Contributions

This research was carried out by equal contribution of all authors.

Availability of data and materials

Research data regarding this manuscript can be shared upon request from corresponding author.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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