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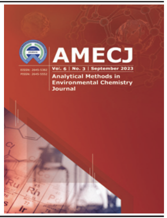

Starch nanocomposite containing hydroxyapatite and eggshell for absorbing methylene blue dye from aqueous solution

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ABSTRACT

Today, polymer nanocomposites (NCs) have become important as suitable candidates for nano absorbents due to their simplicity and cheapness. This research investigated a nano absorbent based on starch nanocomposite containing hydroxyapatite (HA) and eggshell inspired by nature to absorb methylene blue (MB) as a toxic cationic dye from aqueous solution. The effect of temperature, pH, and the ratio of hydroxyapatite and eggshell absorbent on the amount of absorption after immersion in an aqueous medium was measured. The samples were identified by the UV-Vis spectrophotometer, scanning electron microscope (SEM), X-ray energy dispersive spectrometry (EDS), Fourier transform infrared (FTIR), X-ray diffraction (XRD), and BET analysis. Based on the results, the biological nanocomposite of starch-containing 0.125 g hydroxyapatite and eggshell, inspired by nature, has the highest absorption (88%) of methylene blue dye from the aqueous solution quickly. Increasing temperature, increasing pH, and decreasing the amount of nano absorbent increased the absorption of methylene blue dye from the aqueous solution. The results show that starch nanocomposite containing hydroxyapatite and eggshell can absorb methylene blue dye and have good potential for various applications, especially in medical and industrial fields.

1. Introduction

Starch is widely used as a biodegradable, biocompatible, environmentally friendly and non-toxic material with renewable resources [1]. Regardless of its unique properties, starch has limitations such as poor processability, low mechanical properties, poor long-term stability, and high sensitivity to water, which are essential for developing starch nanocomposites. Starch nanocomposites comprise starch polymer as a base and nanometer-scale fillers as reinforcement [2]. Today, bio-based nanocomposites have expanded due to their distinct properties [3, 4]. The starch nanocomposite is a promising starting point for producing materials with environmentally friendly, biodegradable, low toxicity, low cost and biocompatibility properties. The development of new starch-based bio nanocomposites with improved properties has attracted specific applications, including food, agriculture, packaging, environmental remediation, textile, cosmetic, pharmaceutical, and biomedical fields [5, 6]. Hydroxyapatite with the general formula $Ca_{10}(PO_4)_6(OH)_2$ is used as a mineral, green and environmentally friendly adsorbent for wastewater treatment due to its extraordinary ability to absorb

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heavy metal ions, radionuclides, organic pollutants, and fluoride ions. The adsorption mechanisms of this compound include ion exchange reaction, surface complexation, and physical adsorption (such as electrostatic interaction and hydrogen bonding). Therefore, the use of hydroxyapatite nanocomposites has expanded today8 ,7]]. Eggshell has been used as recycled biological waste in the nanoscale to modify nanocomposites with an economical and simple method [9]. Nowadays, nanomaterials have attracted a lot of attention due to their small size and high surface area in various fields such as drug delivery [10], food packaging [11], energy [12], and absorption of dangerous substances [13]. Various physical, chemical, and biological methods have been developed to remove dyes from aqueous solutions (Table. 1). There are different physical methods, such as filtration processes (membrane, nanofiltration, ultra/microfiltration), reverse osmosis, ion exchange, irradiation, electrolysis, coagulation-flocculation, and adsorption to remove dye pollutants from wastewater [14, 15]. Currently, the use of adsorbents is of interest due to their high efficiency, economic feasibility, and simplicity of design for color removal [16]. Investigating the absorption rate of different pollutants is one of the critical applications of nanomaterials based on starch [17, 18], hydroxyapatite [7, 19] and eggshell [20-22]. Therefore, the absorption of starch nanocomposite containing hydroxyapatite and eggshell nanomaterials has been investigated in this research.

Water is one of the most important natural resources in the world for the survival of all living organisms and human growth. Wastewater has harmful effects on water and the environment. As one of the main effluents and pollutants, toxic dyes harm water, environment and living organisms [22]. Therefore, different physical, chemical, biological or combination methods are necessary for water purification [23]. Methylene blue is a heterocyclic molecule with the chemical formula $C_{16}H_{18}ClN_3S$, which is widely used in the pharmaceutical, textile, plastic, leather, cosmetics, and paper industries [24]. Methylene blue is a water-soluble, toxic, carcinogenic and non-biodegradable cationic dye [25]; hence, it can seriously threaten the ecosystem, and human health negatively affects the environment [26, 27]. Recently, methylene blue dye was absorbed by nanomaterials in aqueous solutions in an easy and efficient approach [28, 29]. Nano adsorbents based on starch [30, 31], hydroxyapatite and eggshell are important for methylene removal. Therefore, the importance and innovation of this research is the modification of starch nanocomposite with hydroxyapatite and eggshell to absorb methylene blue dye from aqueous solution as a biological nano absorbent inspired by nature.

2. Experimental

2.1. Reagents and Materials

Starch methylene blue was purchased from Merck (Germany). Hydroxyapatite was prepared from the Technical Research Campus of Yazd (Iran). The eggshell was procured in June 1400 from Sahar Brand Paya Bread Company (Iran). Normal soda solution (NaOH) and standard hydrochloric acid (HCl) were used by CAS numbers 1310-73-2 and 100317, respectively, from Merck Millipore.

Table 1. Comparison of MB removal methods [15].

Method	Techniques
Physical removal	Filtration processes (membrane, nanofiltration, ultra/microfiltration), Reverse osmosis, Ion exchange, Irradiation, Electrolysis, Coagulation-flocculation, Adsorption.
Chemical removal	Non-photochemical: Ozonation, Fenton system. Photochemical: UV light-assisted advanced oxidation process, catalyst-assisted advanced oxidation process, Electrochemical advanced oxidation processes.
Biological removal	Biodegradation of methylene blue dye, Biocatalytic degradation of methylene blue dye.

2.2. Methods

It Includes sample preparation (Eggshell nanoparticles, Starch-hydroxyapatite nanocomposite, Starch-eggshell nanocomposite, and Starch nanocomposite containing hydroxyapatite-eggshell) and general procedure.

2.2.1. Preparation of eggshell nanoparticles

First, the membrane attached to the eggshell was separated and cleaned several times with tap water. Place the washed eggshell in the oven at 105 ºC for two hours until it dries completely. Then, the dry eggshell was powdered and reached the nanometer scale using a ball mill.

2.2.2. Preparation of starch-hydroxyapatite nanocomposite

A 0.5% starch solution was prepared in distilled water. Then hydroxyapatite with ratios of 0.125, 0.25, 0.5 and 0.75% by weight was mixed in the starch solution. Finally, the final nanocomposite was isolated and dried.

2.2.3. Preparation of starch-eggshell nanocomposite

Nanoscale eggshell with ratios of 0.125, 0.25, 0.5 and 0.75% by weight was added to a 0.5% starch solution in distilled water and stirred. Finally, the final nanocomposite was isolated and dried. It should be noted that the nanocomposite with a ratio less than 0.125 was not investigated due to instability.

2.2.4. Preparation of starch nanocomposite containing hydroxyapatite-eggshell

Nanoscale hydroxyapatite and eggshell were added to 0.5% starch solution in distilled water and stirred. Finally, the final nanocomposite was isolated and dried.

2.2.5. Examination of methylene blue dye absorption

First, Landa Max of 3.0 mg L^{-1} (ppm) methylene blue solution was checked by spectrophotometer in the range of 250 to 700 nm, and the wavelength was determined at 664 nm. Then, the samples' absorption rate of methylene blue (3.0 mg L^{-1}) was checked at ambient temperature (25°C). Finally, the changes in temperature, pH of the solution, and the amount of nanosorbent were investigated for the optimal sample. 0.1 standard soda solution and 0.1 standard hydrochloric acid were used to adjust the pH. After shaking and centrifuging the sample (MB), the MB adsorbed on starch nanocomposite containing hydroxyapatite-eggshell at optimized pH and separated by centrifuge system before determination by the UV-Vis spectrometry (Fig. 1).

2.3. Characterization and Instrumental

The samples were investigated by methods of UV-Vis spectrophotometer to study methylene blue absorption, scanning electron microscope to evaluate shape and size, X-ray energy dispersive spectrometry for chemical analysis, Fourier

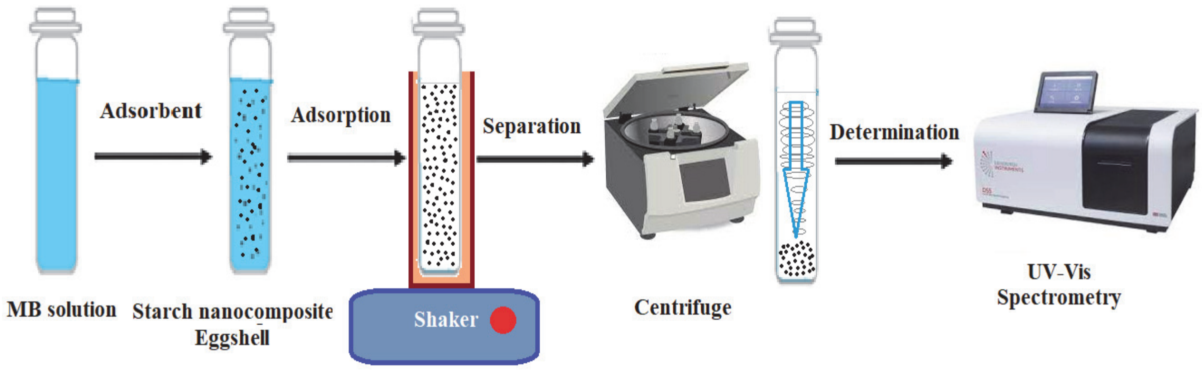


Fig. 1. A schematic diagram of methylene blue dye absorption

transform infrared to determine the functional groups, X-ray diffraction to check the crystal structure, and BET analysis to measure the surface area. In this research, ball mill machines made in Iran to prepare nanoscale eggshells, UV-Vis spectrophotometer PG Instrument model T80 made in Australia to study the amount of methylene blue absorption, scanning electron microscope TESCAN model MIRA lll made by the Czech Republic company with the copper coating to evaluate the shape and size. FTIR of Thermo device Avatar model made in USA by KBr tablets at room temperature to check the functional group. XRD device of Philips model PW1730 made in the Netherlands to determine the crystal structure. BET device of Bel model BELSORP MINI ll made in Japan to measure the surface area.

3. Results and discussions

3.1. Optimization parameters

The absorption percentage of methylene blue dye by 0.1 g of the samples was checked in 5 min (Table 2). Based on the results, eggshell nanoparticles have the highest absorption compared to hydroxyapatite. The nanocomposite has the highest absorption due to the synergistic effect of these compounds, but increasing the ratio of nanocomposite components has decreased the absorption percentage due to the accumulation and reduction of the contact surface. The nanocomposite sample of starch and 0.125 g of hydroxyapatite and eggshell had the highest absorption (88 %) and was chosen as the optimal sample.

Based on the temperature change results for the optimal sample, increasing the temperature up to 35 degrees has no apparent effect on absorption, but increasing the temperature up to 45 degrees has increased movement and absorption (Table 3). Based on the results of pH changes for the optimal sample, its increase caused an increase in absorption. The highest absorption was observed at pH 10, 94% (Table 4). Due to the results of changes in the amount of nano absorbent for the optimal sample, the increase in the amount of nano absorbent probably caused a decrease in absorption due to the increase in accumulation and the reduction in the available surface area (Table 5). Finally, the absorption of methylene blue by 0.0125 grams of starch nanocomposite sample and 0.125 grams of hydroxyapatite and eggshell was investigated as the optimal sample at a temperature of 45 degrees Celsius and a pH of 10, and 98% was calculated as the maximum absorption.

Table 2. Methylene blue absorption rate by the samples.

Sample	Absorption percentage(%)
Eggshell	37
Starch	87
Hydroxyapatite	18
Nanocomposite with 0.125 g of eggshell	75
Nanocomposite with 0.25 g of eggshell	51
Nanocomposite with 0.5 g of eggshell	28
Nanocomposite with 0.75 g of eggshell	33
Nanocomposite with 0.125 g of hydroxyapatite	73
Nanocomposite with 0.25 g of hydroxyapatite	61.2
Nanocomposite with 0.5 g of hydroxyapatite	54
Nanocomposite with 0.75 g of hydroxyapatite	43
Nanocomposite (0.125g eggshell+0.125g Hydroxyapatite)	88
Nanocomposite (0.25 g eggshell+0.25 g Hydroxyapatite)	45
Nanocomposite (0.5 g eggshell+0.5 g Hydroxyapatite)	37
Nanocomposite (0.75 g eggshell+0.75 g Hydroxyapatite)	42

Table 3. Examination of temperature changes on the amount of methylene blue absorption by the optimal sample.

Temperature of solution (°C)	Absorption percentage (%)
25	88
35	83
45	92

Table 4. Examining pH changes on the amount of methylene blue absorption by the optimal sample.

pH	Absorption percentage(٪)
2	48
4	53
7	79
9	86
10	94

Table 5. Examining changes in the amount of nano absorbent on the absorption of methylene blue by the optimal sample.

The amount of Nano absorbent (g)	Absorption Percentage (%)
0.00625	97
0.01250	97
0.0250	95
0.0500	92
0.1000	88
0.2000	84
0.3000	72

3.2. Scanning Electron microscopy and EDS images

The shape and size of samples were checked by scanning electron microscope in Figure 2. It confirmed the results of spherical and uniform nanoparticles with an average nanometer size. Also, the absorption of methylene blue does not affect the shape and size of the nanocomposite.

The X-ray energy dispersive spectroscopy results are shown in Figure 3 and confirm the chemical composition. Based on these results, the elemental analysis of the samples was confirmed.

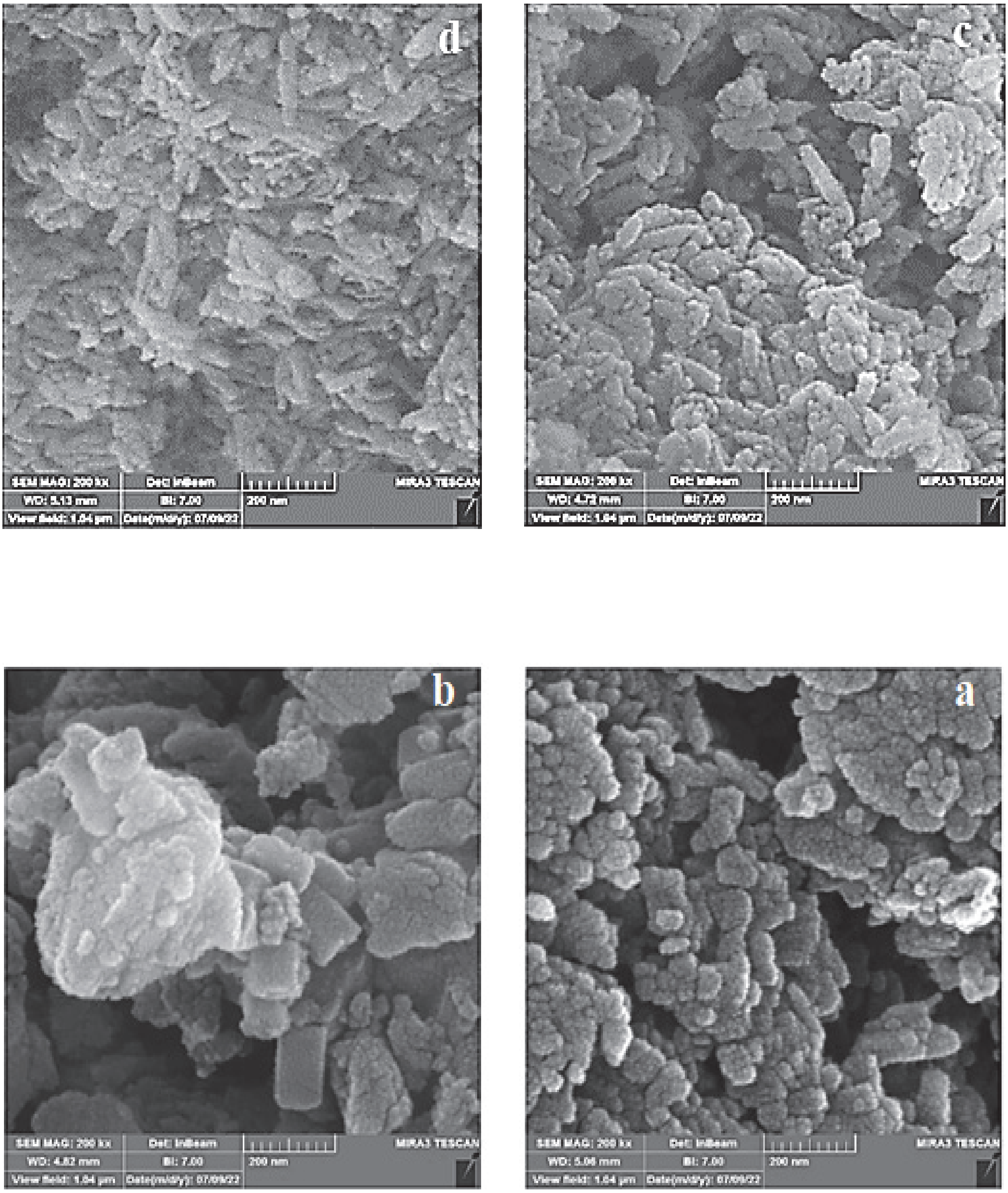


Fig. 2. SEM image of a) hydroxyapatite, b) eggshell, c) optimized nanocomposite before adsorption, and d) optimized nanocomposite after adsorption.

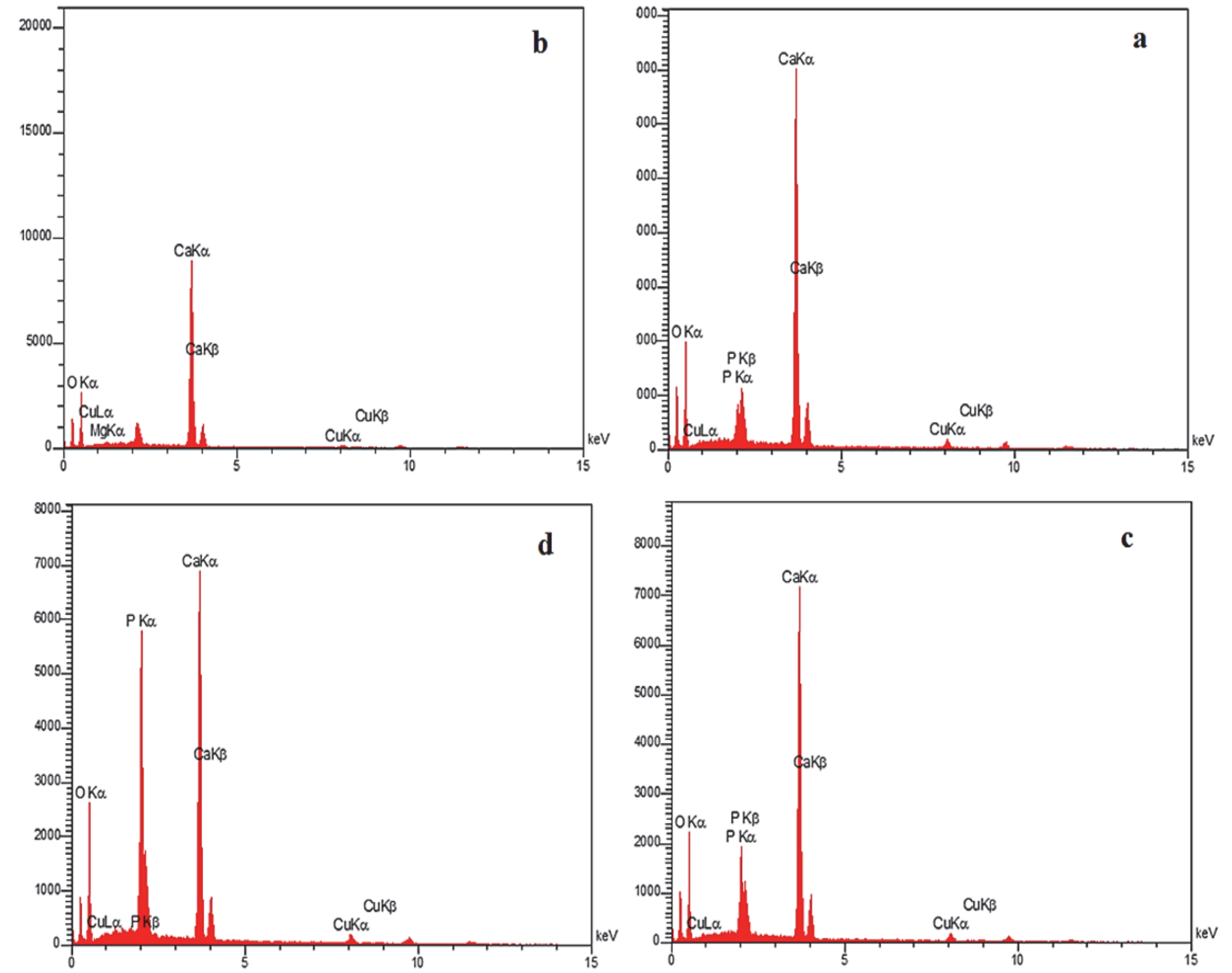
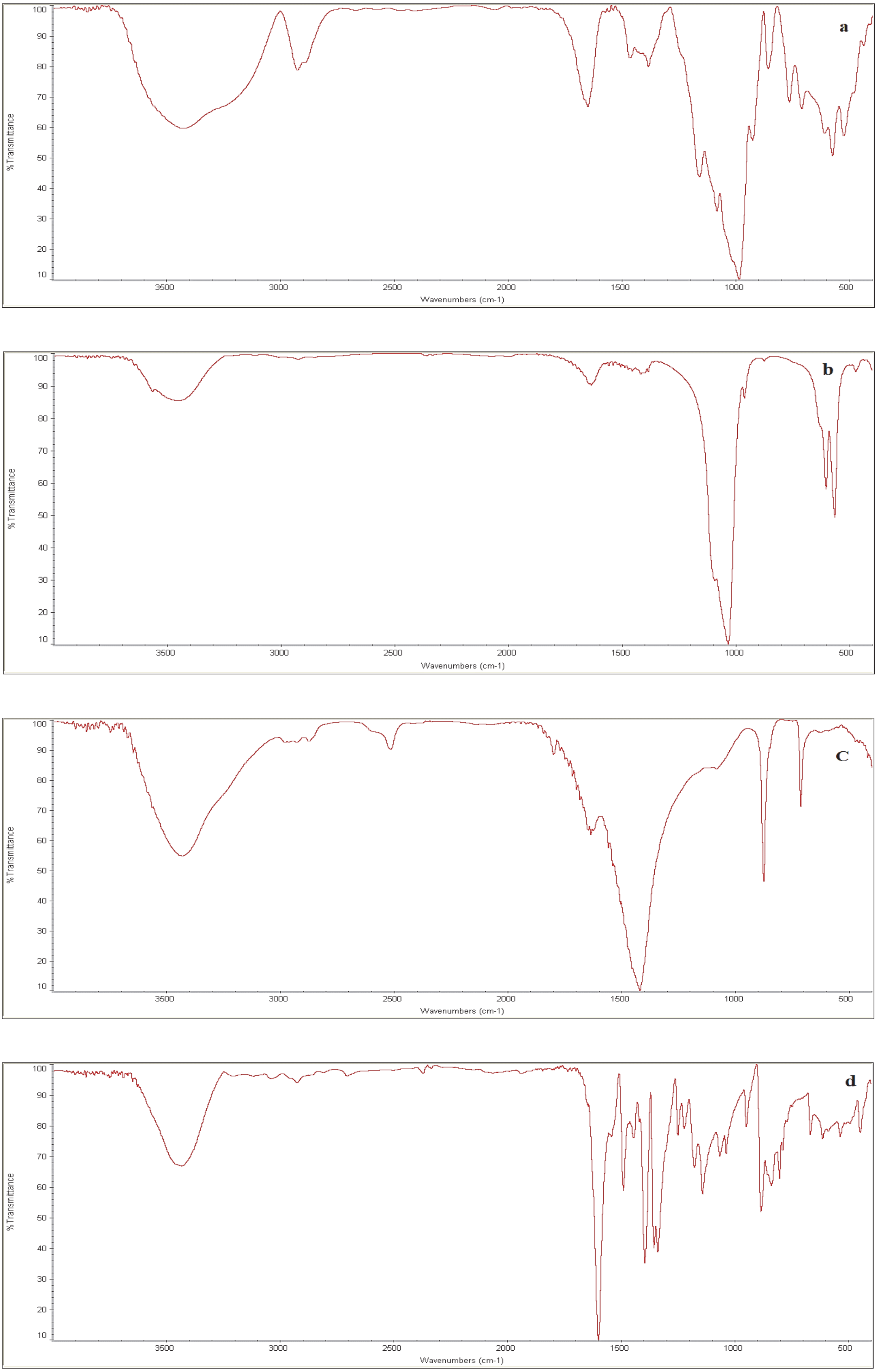


Figure 3. EDS image of a) hydroxyapatite, b) eggshell, c) optimized nanocomposite before adsorption, and d) optimized nanocomposite after adsorption

3.3. FTIR Spectra

The IR absorption spectra of the samples were recorded in the 400–4000 cm-1 range with KBr pellets. FTIR spectrum is shown in Figure 4 to identify functional groups. For starch, the 3000-3700 cm-1 peak indicates the O-H bond, which causes stretching vibrations of intermolecular and intramolecular hydroxyl groups. The peak in the range of 2600-2950 cm^{-1} indicates the C-H bond. The peak in the range of 1500-1800 cm^{-1} indicates the C=O double bond. As shown in the diagram, hydroxyapatite's peak in the wavelength range of 3700-3300 cm^{-1} is related to the O-H bond. The 1000 and 600 cm-1 peak indicates carbonate (CO_3^{-2}) and phosphate (PO_4^{3-}), respectively. For eggshells, the peak in the range of 3500 cm^{-1} indicates the O-H bond. The peak related to C=O and C=C bonds is observed in the 1600-1700 cm-1 range. Considering that a significant part of the eggshell is composed of calcium carbonate, the peaks below 1000 cm^{-1} correspond to CO_3^{-2} in calcium carbonate $CaCO_3$. The peak at 3434 cm-1 indicates O-H and N-H bonds for methylene blue. The CH=N bond is at 1599 $cm^{-1,}$ and the C=C bond is in the 1400-1500 cm-1 range. Peaks in the range of 1300-1400 cm^{-1} correspond to CH_2- and CH_3- and in the range of 1200 cm^{-1} correspond to C-N and N-N, 1176 cm^{-1} correspond to C-H and 1141 cm^{-1} correspond to C–N, and 1066 cm^{-1} corresponds to C–S–C. The FTIR results qualitatively confirm the nanocomposites' functional groups and aggregate peaks.


a
b
C
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% Transmittance
Wavenumbers (cm-1)
100
90
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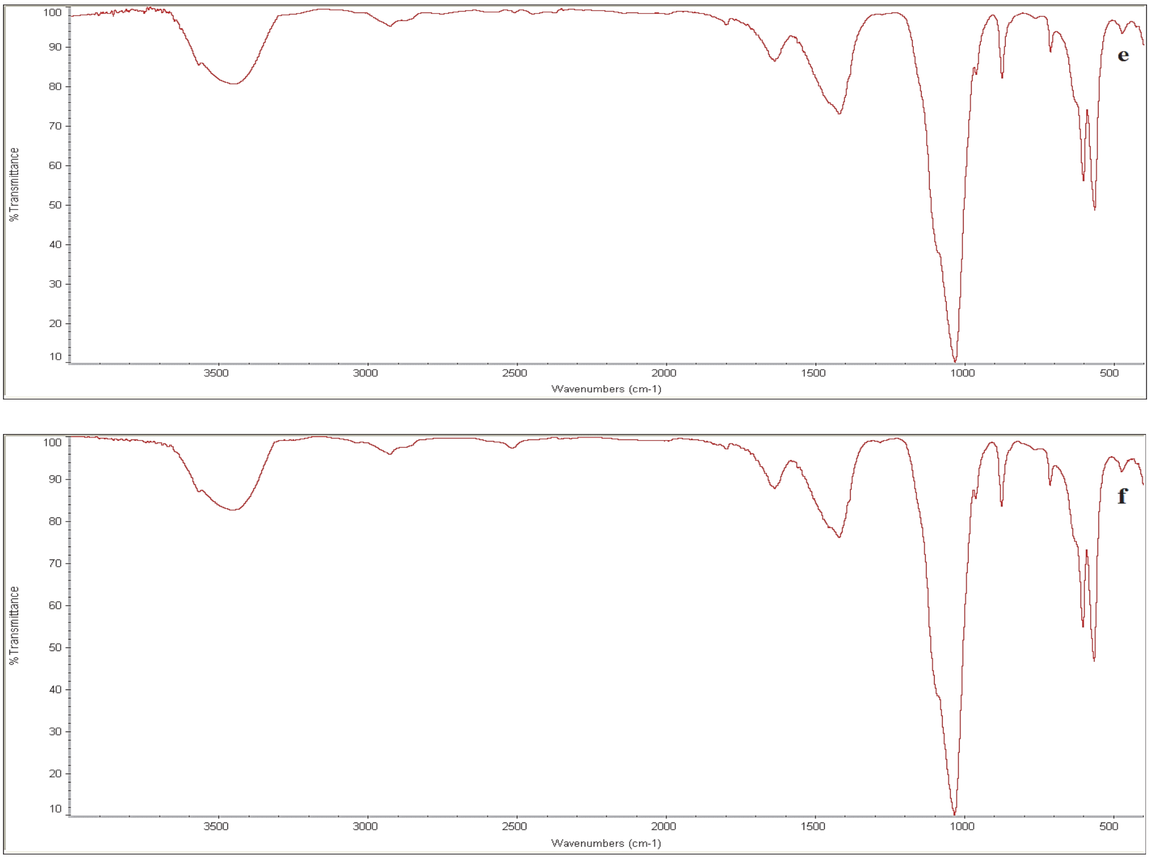

Fig. 4. FTIR spectra for a) starch, b) hydroxyapatite, c) eggshell, d) methylene blue, e) optimized nanocomposite before adsorption, and f) optimized nanocomposite after adsorption.

3.4. XRD pattern

The X-ray diffraction pattern was used to identify the crystal structure in 10° to 70° pairs (Figure 5), which proved the crystalline structure. Based on the results, characteristic peaks of eggshell and hydroxyapatite were observed in the final nanocomposite.

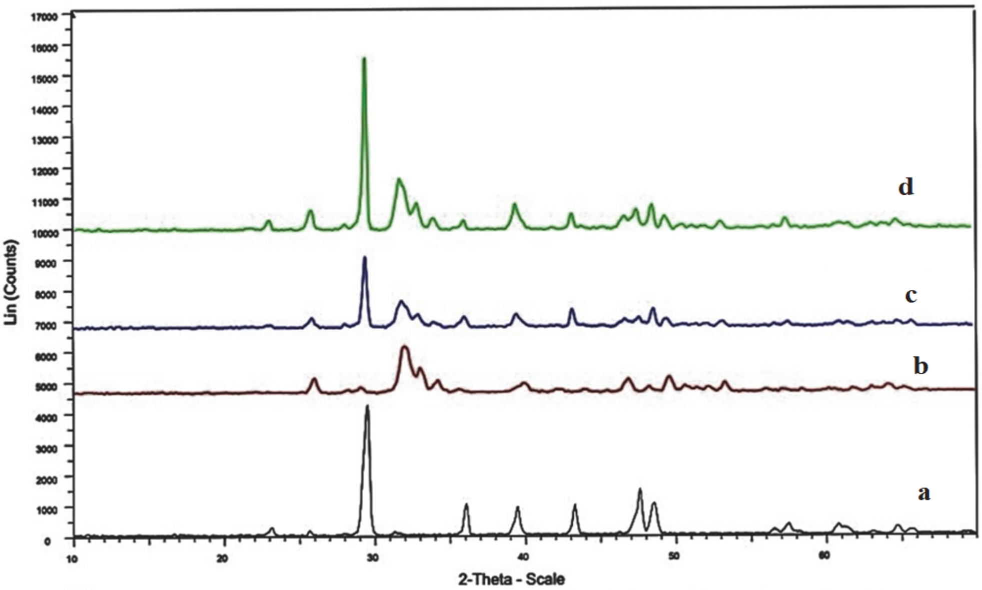

Fig. 5. XRD spectra for a) eggshell, b) hydroxyapatite, c) optimized nanocomposite before adsorption, and d) optimized nanocomposite after adsorption

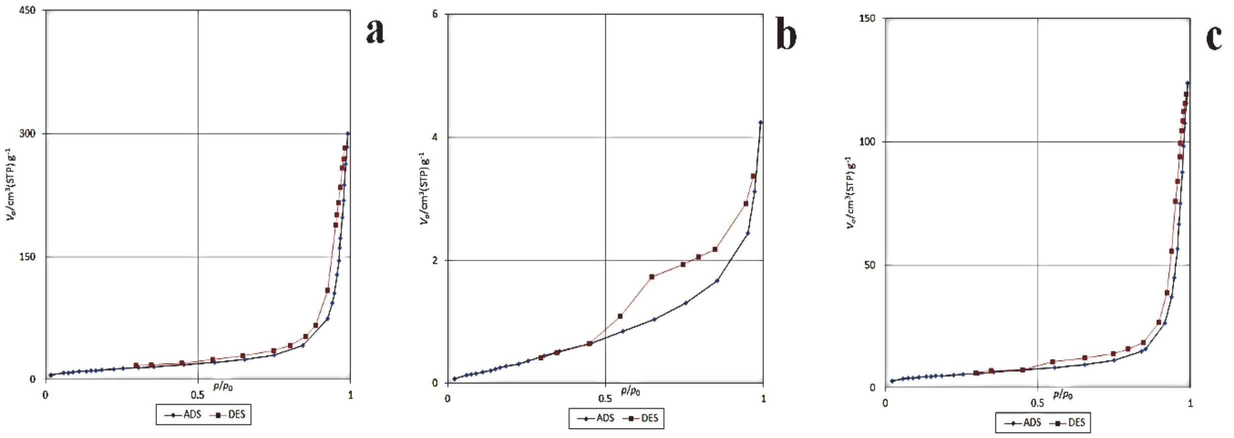

Fig. 6. BET analysis for a) hydroxyapatite, b) eggshell nanoparticles, and c) optimized nanocomposite.

3.5. BET Analysis

The results of adsorption and desorption isotherm to check the surface area are shown in Figure 6. Based on the surface area results for hydroxyapatite, eggshell, and nanocomposite, the optimal surface area is 47.08, 1.27, and 18.85 m^2 g^{-1}, respectively. In other words, hydroxyapatite has the largest surface area, which is confirmed by SEM results and the smaller size of nanoparticles.

3.6. Discussion

The spectrophotometer results showed that the nanocomposite of starch and 0.125 g of hydroxyapatite and eggshell have the highest absorption of methylene blue dye from the aqueous solution. In general, the increase in the percentage of nanocomposite components due to the decrease in the available surface has caused a reduction in the absorption percentage. Temperature changes have no noticeable effect on absorption. An increase in pH causes an increase in absorption due to more active sites, a decrease in the competition between positive charges and an increase in the adsorption of methylene blue through electrostatic attraction. These results confirm the previous report [32]. As a result, many OH- are available on the surface, and the adsorbent surface tends to be negatively charged. Hence, the affinity for exchanging OH^- ions with the cationic dye solution increases [33]. Based on the SEM results, hydroxyapatite was observed as spherical nanoparticles with an average size of 49 nm, eggshell spherical nanoparticles with an average size of 100 nm, and the presence of nanoparticles in the optimal nanocomposite before and after absorption was observed. Based on EDS results, oxygen (O), phosphorus (P) and calcium (Ca) elements were observed in hydroxyapatite [34] and oxygen, magnesium (Mg) and calcium in eggshells [35], according to other reports. FTIR results confirm the functional groups of starch [36], hydroxyapatite [37], eggshell [38], and methylene blue [39] based on previous reports. In the XRD pattern of hydroxyapatite, the peaks at 2θ are 26º, 32º, and 33º corresponding to the crystal plane (102), (211), and (300) according to the JCPDS standard card (896438) [40]. The high percentage of eggshell is composed of $CaCO_3$ and the 2θ peaks are equal to 29.1, 35.7º, 39.3º, 43.7º and 48.3º corresponding to the crystal plate (104), (110), (113), (202) and (116). The composition of $CaCO_3$ is according to the standard card 1934-002-99.

4. Conclusion

The optimal sample of starch nanocomposite and 0.125 g of hydroxyapatite-eggshell with 0.1 g and the pollutant concentration of 3 ppm showed absorption of 88% in 5 min. Based on the results, the optimal starch nanocomposite containing hydroxyapatite and eggshell nanostructures has the potential to absorb dye due to the small size of these compounds. Generally, increasing temperature, increasing pH and decreasing the amount of nano absorbent has increased the absorption percentage of methylene blue dye from the aqueous solution. SEM confirmed the nanostructures for size and shape, EDS for elemental analysis, FTIR for functional groups, XRD for crystal structure, and BET for surface area. Therefore, the advantage of this bio-nano sorbent is a simple, fast and cheap preparation method with high dye absorption in a short time. Based on the results of this nanocomposite inspired by nature, it can show the future prospect of expanding research in various industries more than in the past.

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