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ARTICLE

SYNTHESIS OF CELLULOSE/ZIRCONIUM OXIDE NANOCOMPOSITE AND THE STUDY OF ITS ACTIVITY IN THE REMOVAL OF POLLUTANTS

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ABSTRACT

In this research, the cellulose/zirconium oxide nano composite was successfully synthesized. In the preparation of this nano composite, zirconium (IV) tert-butoxide and stearic acid were used as the sources of zirconium and complexing agent of cellulose, respectively. The structure of this nano composite was studied using Fourier transform infrared spectroscopy (FT-IR) analysis, and X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods were applied to investigate the size and morphology of particles, respectively. Zirconium dioxide nanoparticles with the average size of 50 nm were obtained as the pure nano composite with cellulose and the sizes ranged from 31.9 to 46.3 nm. To study the catalytic activity of prepared nano composite, malachite green was used as one of the environmental pollutants. The effect of pollutant and adsorbent concentration, time, and pH was investigated, and the optimal conditions were determined for the removal of pollutants.

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KEY WORDS
Nanocomposite, Cellulose, Zirconium oxide, Malachite green, Catalytic activity

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INTRODUCTION

Water, as the most vital fluid, covers more than three-quarters of earth surface. Nowadays, the limited resources of available fresh water are at the risk of microbial and chemical contamination, and many pollutants seriously threaten the vital resources for humans through industrial wastewater and fertilizers. Clean water (water without toxic chemicals and pathogens) is essential to human health. Also, clean water is considered as the vital pure substance in different main industries such as electronic, drug, and food. The world faces many challenges in increasing demand for clean water as fresh water resources [1-4]. Numerous issues related to the water quality can be improved using nanoparticles, nano filtration, or other product of nanotechnology. Innovation in the development of new technologies for making fresh water is considered as one of the most significant technologies. Using special nanoparticles placed in membranes or in the structure of filters purifies unusable drinking water obtained from institutes and factories in an effective, low-cost and quick way [5-7]. Nano materials have a great surface area compared to the materials with large scale. In addition, these materials can interact with different chemical groups in order to increase their affinity with especial compounds. Also, nano materials can be considered as the recoverable ligands with great capacity and selectivity for the toxic metal ions of radionuclides, organic and mineral solvents. Adsorbents are widely used as separators in the water purification and removal of organic pollutants such as malachite green from the polluted water. Malachite green is a triaryl methane dye which widely used in the textile industry for dyeing silk, leather, cotton, wool, and hemp. This substance is also applied as bactericide, fungicide, and parasiticide in the aquaculture industry. Due to the properties of malachite green, its removal from the aqueous solutions is difficult, and it is also toxic to many microorganisms [8-11]. Different methods have been reported for the removal of this substance from aqueous solution that using adsorbents with the adsorption ability of this substance can be considered as one of the effective methods [12, 13]. In 2014, Vinod et al. used pectin zirconium(IV)selenotungsto phosphate (PC/ZSWP) nano composite adsorbent, prepared via the sol-gel procedure, for removal of the methylene blue (MB) and malachite green (MG) in different conditions. The adsorption percentages of this photo catalytic nano composite for methylene blue and malachite green in the presence of light in 3 hours were 89.21 and 79.27%, respectively, which were higher than the adsorption of this photo catalyst in darkness. In 2014, Jing and co-workers synthesized a suitable adsorbent for removal of fluoride ions from the aqueous systems using sodium carboxy methyl cellulose saturated with Zr(IV) or CMC-Zr. They achieved the maximum adsorption capacity of this adsorbent by varying pH, temperature, the fluoride concentration, the amount of adsorbent, and the contact time. This spontaneous and endothermic process is in agreement with the Langmuir and Freundlich isotherm models. In this process which occurs through exchanging the sodium ions of adsorbent with fluoride ions, CMC-Zr can be a suitable adsorbent for removal of fluoride from the aqueous solutions [14]. In 2013, Rifaqat et al. applied graphene to increase the adsorption capacity of zirconium oxide ($ZrO2$) nano composite adsorbent, and successfully removed 4-chlorophenol from the aqueous systems in high yields. Investigating the effect of temperature, concentration, contact time and pH showed the spontaneous and endothermic process, and the maximum adsorption took place at pH 1. Also, using the mixture of methanol and sodium perchlorate (0.1 M) (40:60) led to increasing the removal percentage of 4-chlorophenol to more than 90% [15]. The new aspect and innovation of this research is that the cellulose/zirconium oxide nano composite has been used for the first time as an adsorbent in the removal of pollutants. To prepare these nanoparticles, sol-gel method was applied due to its simple procedure and controllability of the shape of obtained nanoparticles.

MATERIALS AND METHODS

Materials

Zirconium (IV) tert-butoxide, cellulose, stearic acid, malachite green, sodium hydroxide, hydrochloric acid, and acetone were purchased from the Merck company in Germany. Deionized water was used in the experiments.

Instruments

The Fourier Transform Infrared spectrometry (FT-IR) device with the model of PerkinElmer Spectrometer RX1FT-IR was used to confirm the synthesized nanoparticles. The size of nanoparticles was determined by X-Ray Diffraction (XRD) instrument with (XRD)PTS 3003 model. Scanning electron microscopy (SEM) device with EM 3200 model, made by KYKY Company, was performed for investigating the structure and morphology of samples. The adsorption of samples and their pH were measured using Perkin Elmer UV/Vis 25 spectrophotometer and METTLER TOLEDO pH meter, respectively.

Methods

Preparation of zirconium dioxide nanoparticles

Stearic acid (569 g, 2 mol) was melted in a beaker at 73 ☐C, then, zirconium (IV)tert-butoxide (383.7 g, 1 mol) was added to the mixture and stirred using a magnet. Afterwards, the mixture was heated in an oven at 300 and 400 ☐C for 60-70 min, and all impurities related to the stearic acid were taken out as H2O, CO2, and CO. Then, the temperature increased to 850-900 ☐C for calcination, and remained fixed for 5 hours. After the completion of this step, the mixture was cooled, and zirconium dioxide nanoparticles were obtained.

Preparation of cellulose-zirconium dioxide

Cellulose (4.5 g) and zirconium dioxide (0.5 g) (cellulose: zirconium, 90:10) were poured in a beaker, and some acetone amount of was added as the solvent. Then, the mixture was heated and stirred using a magnet. After drying the mixture by heating, the cellulose/zirconium nano composite was achieved.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of zirconium dioxide

[Fig. 1] illustrates the FT-IR spectra of pure synthesized zirconium dioxide nanoparticle. It shows the structural properties of nanoparticle. Two peaks at 517.88 and 618.06 cm-1 demonstrate the vibrations of Zr-O in tetragonal zirconium oxide.

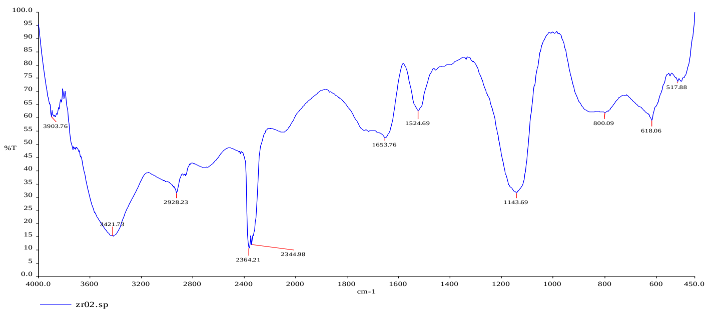


Fig. 1: FT-IR spectra of pure zirconium dioxide nanoparticle.

FT-IR spectra of pure cellulose

As depicted in [Fig. 2], absorption band at 3421.91 cm-1 shows stretching vibration of OH groups present in the cellulose structure.

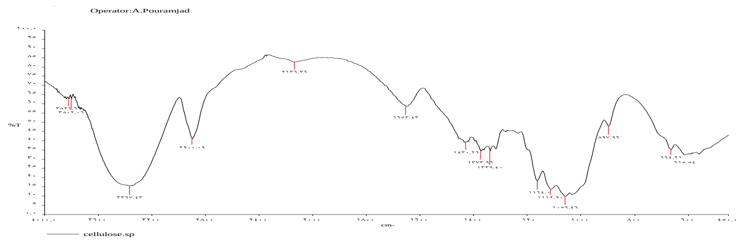


Fig. 2: FT-IR spectra of pure cellulose.

FT-IR spectra of cellulose/zirconium dioxide nano composite

[Fig. 3] presents the FT-IR spectra of cellulose-zirconium dioxide nano composite. In fact, it shows the structural properties of nano composite. Two peaks at 517.88 and 618.06 cm-1 depict the vibrations of Zr-O in zirconium oxide, and the absorption band at 3421.91 cm-1 illustrates the stretching vibration of OH groups present in the cellulose structure.

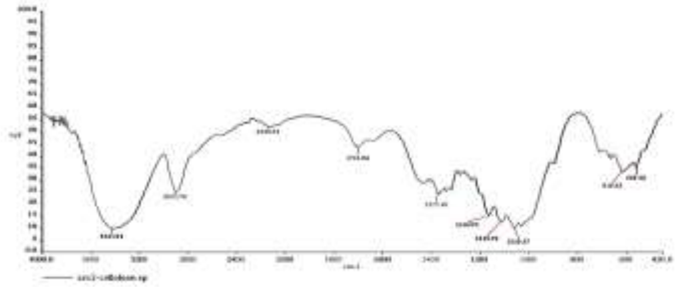


Fig. 3: FT-IR spectra of cellulose-zirconium dioxide nano composite.

XRD spectra of cellulose-zirconium dioxide nano composite

[Fig. 4] depicts the XRD image of zirconium dioxide nanoparticles. According to the obtained results, the prepared nanoparticle is cubic which is completely in agreement with the single crystal XRD. To calculate the average size of crystalline particles based upon the XRD spectra, Debye-Scherrer equation was used as follows [16]:

Equation 1: $\tau = \frac{K\lambda}{\beta cos\theta}$

Where k is a constant amount equal to 0.89; λ is X-ray wavelength equal to 0.154056; β is the width of peak at half the maximum, and θ is the half of diffraction angle.

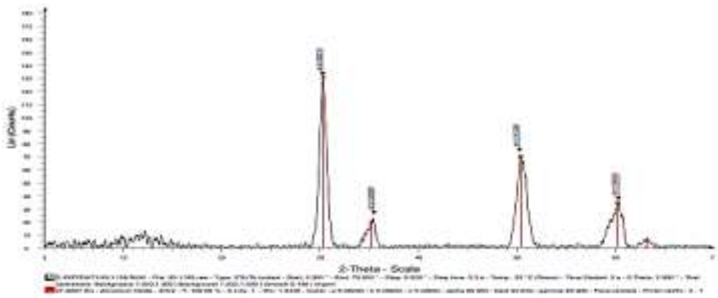


Fig. 4: XRD spectra of cellulose-zirconium dioxide nano composite.

Scanning electron microscopy (SEM)

SEM spectra of zirconium dioxide nanoparticle

As illustrated in [Fig. 5], SEM image shows the morphology of zirconium dioxide nanoparticles. These nanoparticles were distributed spherically throughout the sample. Zirconium dioxide nanoparticles are observable with the size of 50 nm.

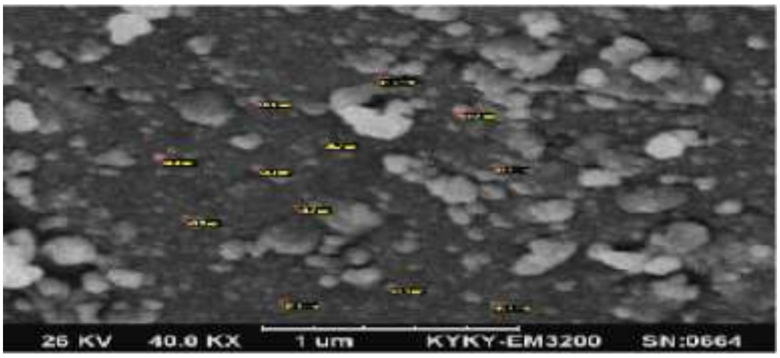


Fig. 5: SEM image of zirconium dioxide nanoparticle.

SEM spectra of cellulose-zirconium dioxide nano composite

The morphology of synthesized nano composite was studied using SEM analysis. As can be seen from [Fig. 6], zirconium dioxide nanoparticles were distributed on the cellulose surface as a substratum. The size of particles was in the range of 31.9 to 46.3 nm. The size of the smallest particle of zirconium dioxide is 31.9 nm. The appropriate homogenity and distributaion of particles are observable in SEM image.

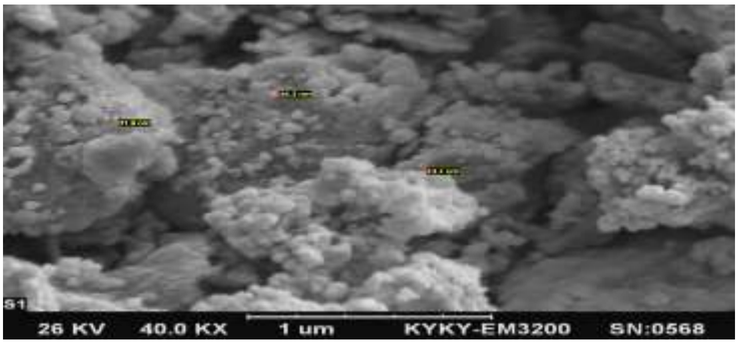


Fig. 6: SEM image of cellulose-zirconium dioxide nano composite.

Investigating the catalytic activity of cellulose-zirconium dioxide nano composite

To investigate the catalytic activity of cellulose-zirconium dioxide nano composite, malachite green was used as a pollutant. The effect of different parameters such as the amount of adsorbent, pH, the concentration of malachite green, and time was studied.

The calibration graph of malachite green adsorption versus its different concentrations

To measure the concentration of MG, the absorption properties of this substance in UV-Vis region were used. Also, to determine the maximum wavelength in the range of 350-800 nm using double-beam spectrophotometer instrument, the adsorption graph was drawn for different concentration of malachite green (1-10 ppm). As presented in Scheme 7, malachite green has the maximum adsorption at wavelength of 625 nm. As a result, this wavelength was chosen for the measurement of malachite green concentration.

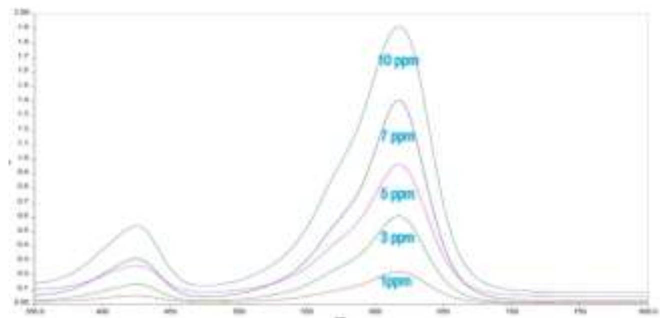


Fig. 7: UV-Vis spectra of MG solution (0-10 ppm).

The calibration graph is essential for determining the concentration of samples which their color were removed by the adsorbent. So, different concentrations of malachite green were prepared, and their adsorption was measured at the wavelength of 625 nm. The calibration graph, depicted in [Fig. 8], was drawn based upon the results of [Table 1].

Table 1: The changes of malachite green concentration and adsorption

Adsorption	MG concentration
0.1976	1
0.6014	3
0.9742	5
1.3745	7
1.9104	10

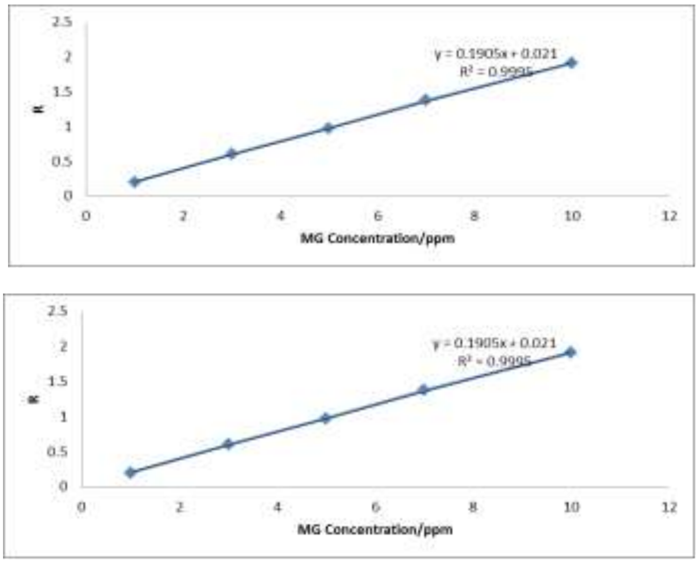


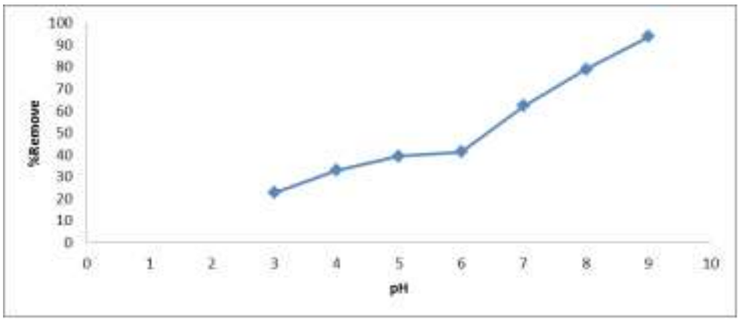
Fig. 8: The diagram of malachite green concentration versus different concentrations.

To calculate the removal percent, equation 2 was used in different experiments:
Equation 2:

$$\text{Removal Percent} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2)$$

The study of optimal pH for the malachite green removal

One of the main parameters for the adsorption and removal of color pollutant is pH. To investigate and evaluate the effect of pH on the removal of malachite green from aqueous solutions, some experiments were conducted in different pH under the constant conditions of other parameters. As illustrated in [Fig. 9], the suitable pH for removal of color is 9.



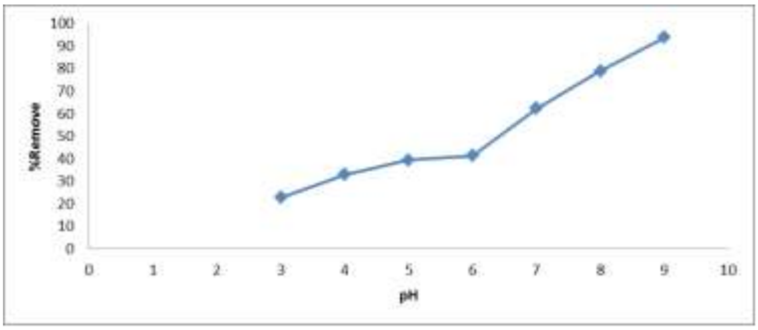


Fig. 9: The diagram of pH for removal of malachite green.

Studying the removal percentages of malachite green according to the amount of cellulose-zirconium dioxide nano composite adsorbent

The increase of adsorbent raises the adsorption percentage or color removal. In fact, by increasing the amount of adsorbent, the available sites for adsorption was increased, so the color removal increases. If the amount of adsorbent is more than the optimized amount, overlapping the sites of adsorbent molecules decreases the adsorption. The optimal amount of adsorbent for removal of pollutant from the system is 0.7 g.

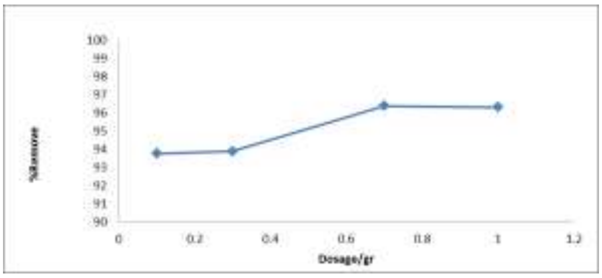


Fig. 10: The diagram of optimal amount of adsorbent for malachite green removal.

Investigating the removal percentages of malachite green based upon time

According to the diagram, rising time increases the removal percent. The highest removal percent occurs at t = 80 min. After t = 80 min, the removal percentage of malachite green decreases slightly.

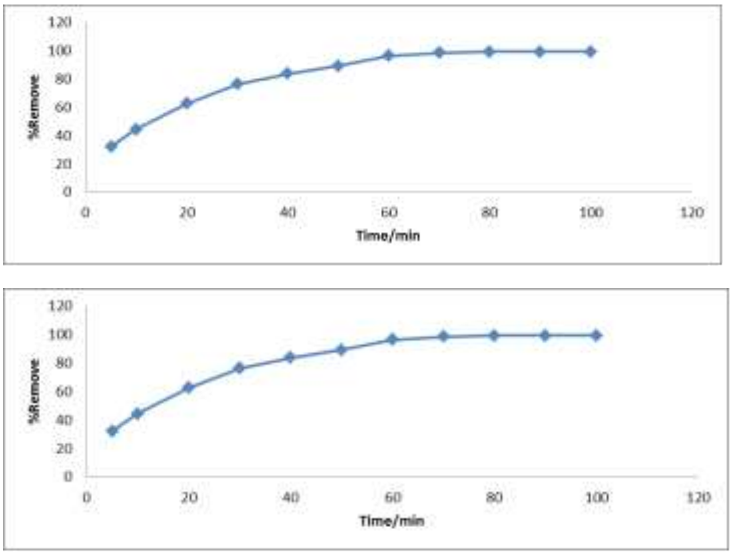
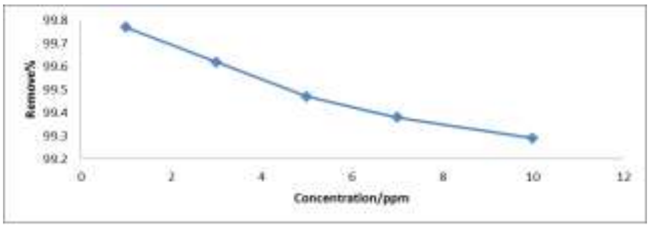


Fig. 11: The diagram of optimal time for removal.

Investigating the removal percentages of malachite green with different concentrations under the optimized conditions

[Fig. 12] shows the diagram of removal percent versus pollutant concentration under the optimized conditions (pH = 9, t = 80 min using 0.7 g of adsorbent). Increasing the initial concentration of color decreases the adsorption percent. The initial concentration is a driving force for overcoming the resistance of all dyes between aqueous and solid phases. As illustrated in Fig. 12, raising the concentration of dyes decreases the removal percent.



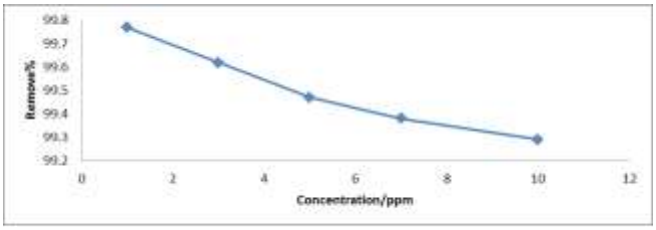


Fig. 12: The diagram of removal percent versus pollutant concentration.

CONCLUSION

The cellulose-zirconium dioxide nanoparticle was successfully synthesized. To investigate the catalytic activity of this nanoparticle, malachite green was used as a pollutant. The effect of various operating parameters on the malachite green removal was studied. The results showed that the highest percentage of removal occurs at pH = 9 and t = 80 min using 0.7 g of adsorbent and 10 ppm concentration of pollutant.

CONFLICT OF INTEREST

There is no conflict of interest.

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FINANCIAL DISCLOSURE

None

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