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Investigating the Removal Efficiency of Steroid Drugs Using Magnetized Bentonite Nanocomposite

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ABSTRACT

With the increase in population, emerging chemical pollutants such as pharmaceutical compounds have entered water sources that conventional water purification methods cannot completely remove. Therefore, it is necessary to remove them considering the dangers of these pollutants and their toxicity to the environment and human society. In this research, iron oxide-magnetized bentonite nanocomposite was synthesized in situ using the co-precipitation method to remove acetaminophen from water sources. The structure of the synthesized nanocomposite was investigated using FTIR, BET, XRD, EDX and FSEM analyses and its performance in acetaminophen removal was studied. The results showed that the synthesized iron oxide-magnetized bentonite nanocomposite has an appropriate performance (100% in 30 min) in the process of acetaminophen removal. The test conditions (nanocomposite amount, time, pH and acetaminophen concentration) were optimized. The highest amount of acetaminophen removal was obtained by using iron oxide-magnetized bentonite nanocomposite with a reaction time of less than 30 min, pH= 4, initial acetaminophen concentration of 25 mg/L and adsorbent concentration of 1 g/dL.



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Introduction

With the increase in population, compounds such as medicinal compounds, antibiotics and cosmetics are widely used all over the world. Medicinal compounds are considered one of the most important emerging pollutants, which are important to improve the level of health and safety of society and preserve water resources due to their complex chemical structure, long shelf life against decomposition and the toxicity of their removal. These compounds can be discharged directly as pharmaceutical industries' wastewater discharge, or indirectly as household and hospital wastewater into municipal raw sewage and sewage treatment plant systems [1]. They may be used in the form of liquid fertilizer, activated sludge or soil amender in agriculture, and then released into the aquatic environment, soil, drinking water and food chain. Therefore, the partial presence of pharmaceutical pollution in the aquatic environment is known as one of the challenges of the emerging pollutants in the environment. Acetaminophen with the chemical formula $C_8H_9NO_2$ is a drug widely used without a doctor's prescription as a non-narcotic, pain killer and fever medicine with a solubility of 12900 mg/L. In addition to urine and faeces, acetaminophen enters urban sewage by spreading from drug production sites discharging its excess directly. 58 to 68% of it leaves the human body and enters the sewage treatment plants without any changes and can remain in the environment for 15 days without decomposition resulting in many environmental hazards [2]. These substances are biologically active, so even their low concentrations should not be ignored because their ability to accumulate in water sources leads to destructive and serious effects on human health and organisms in the water and soil environment [3]. Nowadays, research on the removal of these compounds with different methods is being followed seriously because they are not completely removed, or their removal is incomplete using conventional methods of water purification. Chemical and electrochemical removal methods, ion exchange, advanced oxidation, coagulation and surface adsorption are used to remove these compounds [4]. Surface adsorption is one of the most efficient methods because of its simple operation, high efficiency and low cost [5]. The performance of the surface adsorption method is influenced by the characteristics of the adsorbent. The adsorbents that are usually used to remove the pollutants from the wastewater have characteristics such as thermal stability and a unique network structure in molecular size and ion exchange [6]. Nanostructures are combined with suitable adsorbents to make magnetic nanocomposites with an appropriate adsorption capacity and significant magnetic properties as adsorbents. Adding nanostructures to the structure of adsorbents can improve their reusability, mechanical properties, thermal stability, stability under environmental

conditions, magnetic responses and efficiency. It also increases the active sites of the adsorbent for absorption by increasing the contact surface and porosity and providing different functional groups, which in turn cause the adsorbent to have stronger interactions with the target molecules in a shorter time [7; 8].

The statement of the problem, innovation and objectives

In the present research, the efficiency of iron oxide-magnetized bentonite nanocomposite to remove acetaminophen from urban wastewater was studied in two stages. First, the magnetized bentonite nanocomposite adsorbent was synthesized, and then the efficiency of acetaminophen removal was studied using the nanocomposite. Next, the effect of different parameters such as pH, reaction time, the amount of adsorbent and initial concentration of acetaminophen on acetaminophen removal was investigated. Figure 1 shows the schematic view of the conducted process in the present research.

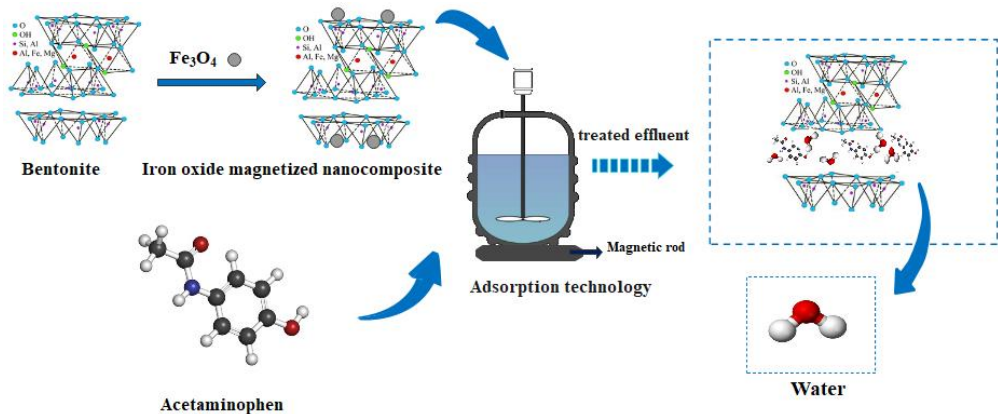


Figure 1. Schematic view of the conducted process in the research.

Methodology

The used raw materials were bentonite nano clay ($H_2Al_2O_6Si$), 6-hydrate ferric iron chloride ($FeCl_3 \cdot 6H_2O$), 4-hydrate ferric iron chloride $FeCl_2 \cdot 4H_2O$, ammonium hydroxide (NH_4OH), sodium hydroxide ($NaOH$), sodium chloride ($NaCl$), hydrochloric acid (HCl) and acetaminophen ($C_8H_9NO_2$) prepared by Merck Company for the synthesis of iron oxide magnetized bentonite nanocomposite to remove acetaminophen.

XRD, BET, EDX, FTIR and FESEM analyses were used to determine the properties of the synthesized magnetic nanocomposite. Nitrogen gas absorption and desorption analysis (BET analysis) were used with Quantchrome (chambert 3000) device to measure the surface area, pore volume and pore size dispersion

of synthesized nanoparticles. Infrared spectrometry (FTIR) analysis was conducted using Unicam 4000 to identify the functional groups on the surface of the nanocavity. X-ray diffraction (XRD) analysis was carried out using a Panalytical Xpert PRO X-Ray Diffractometer (Xpert Pro MPD model) to identify the crystal structure of the sample. Field emission scanning electron microscope (FE-SEM) analysis was used which led to the electrical conductivity, repelling surface electrons and the increase of image resolution.

In this research, a synthetic solution of 1000 mg/L of acetaminophen was prepared by dissolving one gram of acetaminophen in 1000 ml of double-distilled water to investigate the removal efficiency of acetaminophen using the studied process. Acetaminophen concentrations of 25, 50 and 75 mg/L were obtained by diluting with the ratios of 1 to 40, 20 and 3.13. A glass pilot reactor of a discontinuous regime was set up to investigate the removal of acetaminophen in the states of bentonite nanoparticles and iron oxide-magnetized bentonite nanocomposites. Experiments to determine the optimal conditions for removing acetaminophen were conducted under laboratory conditions. The optimal conditions were given as the concentration of iron oxide nanoparticles (6-18%), contact time (30-90 min), pH (4-9), the concentrations of bentonite nanoparticles (0.5 to 1.5 g/dl), iron oxide-magnetized bentonite nanocomposite (6, 12 and 18%) and acetaminophen (25, 50 and 75 mg/liter) in urban water. One milliliter of water inside the reactor was tested at the end of each stage of the experiments to determine the removal efficiency of the sampling process. The experiment was performed after filtering by a membrane filter with the size of 0.45 microns using a spectrophotometer at a wavelength of 400 nm with a calorimetric method according to the instructions of the synthesis process. The synthesis process of iron oxide-magnetized bentonite nanocomposite containing 6, 12 and 18% magnetite was performed by co-precipitation method and in situ.

Results and discussion

Spectroscopic analysis is one of the most important and common spectroscopic techniques to identify and measure functional groups, metal groups, and OH bonds on the surface of compounds. In the present study, FT-IR spectroscopy was used to investigate the functional groups, and the bands present in the synthesized iron oxide-magnetized bentonite nanocomposite.

The distribution of particles is essential for determining the characteristics of catalysts. Scanning Electron Microscope (FESEM) is one of the best devices available to analyze the morphology of nanostructures and particle distribution. For this reason, the morphology of iron oxide-magnetized bentonite nanocomposite was evaluated in Figure 2 using a scanning electron microscope.

The micron particles of the adsorbent are clearly shown in the SEM arc. The pore diameter of 42.8 to 67.5 nm represents the predicted absorption of acetaminophen molecule on the adsorbent surface of magnetic iron oxide bentonite nanocomposite.

X-ray diffraction (XRD) analysis is a method to study the crystal structure of materials and the size of crystals. It is possible to determine the atomic structure and crystal characteristics of the materials using this information. In this way, it is possible to determine the type and structure of the sample. XRD pattern obtained from iron oxide-magnetized bentonite nanocomposite is shown in Figure 3. The pure peaks of relatively uniform structures, layered uniform structures with small ridges, and non-uniform and spherical structures are respectively displayed for magnetite nanoparticles, bentonite and iron oxide-magnetized bentonite nanocomposite. The crystal size of magnetite nanoparticles, bentonite and iron oxide-magnetized bentonite nanocomposite can be calculated based on the Debye Scherrer formula, which was given as 20, 1 and 48 nm, respectively. Output peaks at 80° angle were consistent with the standard peaks of iron oxide-magnetized bentonite nanocomposite. Therefore, the purity of iron oxide-magnetized bentonite nanocomposite was confirmed. The peak of iron oxide-magnetized bentonite nanocomposite was at 80° to 85.4° 2θ and the peak of magnetite was at 56.35° 2θ. Therefore, these peaks represent quartz (silicates) as the main composition of iron oxide-magnetized bentonite nanocomposite.

X-ray Energy Diffraction (EDX) spectroscopy is an analytical method to analyze the structure or chemical properties of a sample and determine the percentage of elements in solid samples. A field emission scanning electron microscope equipped with EDX with 30000 magnification was used to determine the shape of the iron oxide-magnetized bentonite nanocomposite. The weight percentages obtained from the elemental analysis of magnetite, bentonite and iron oxide-magnetized nanocomposite are presented in Table 1.

Table 1. Elemental analysis weight percentages of iron oxide-magnetized bentonite nanocomposite.

Iron oxide magnetic bentonite nanocomposite		Bentonite		Magnetite	
Weight(L)	element	Weight(L)	element	Weight(L)	element
50/8	SiO ₂	5/5	CaCO ₃	8/6	Mn
28/2	Fe ₃ O ₄	57/0	SiO ₂	0/2	Cr
13.9	Al ₂ O ₃	23/6	Al ₂ O ₃	14/2	SiO ₂
2/6	K ₂ O	4/6	Ti ₂ O	0/1	K ₂ O
0/5	CaO	3/8	Fe ₃ O ₄	2/3	CaO

Iron oxide magnetic bentonite nanocomposite		Bentonite		Magnetite	
Weight(L)	element	Weight(L)	element	Weight(L)	element
1/4	Na ₂ O	5/5	MgO	74/6	Fe ₃ O ₄
1/1	MgO	100	Sum	100	Sum
100	Sum				

The results showed that the nanoparticles have a non-uniform and quasi-spherical shape, and the minimum diameter of the particles is 2.48 nm. Iron oxide- magnetized bentonite nanocomposite consists of elements including silicon (Si) as the main element and iron (Fe) as the minor element. Very fine particles lead to an increase in the porosity and surface area of iron oxide-magnetized bentonite nanocomposite. EDX analysis of the microspores' surface confirms the XRD pattern.

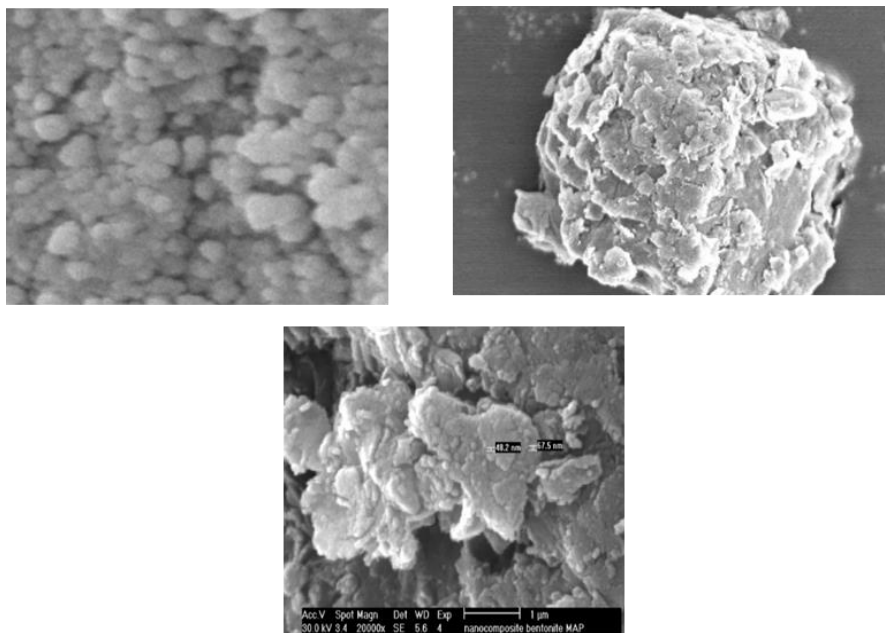


Figure 2. SEM analysis of magnetized iron oxide nanocomposite.

The effect of pH on the acetaminophen removal process by iron oxide-magnetized bentonite nanocomposite

The effect of pH on the removal process of acetaminophen was investigated in the presence of iron oxide-magnetized bentonite nanocomposite at pH = 4, 7 and 9 in the concentrations of 25 to 75 mg. As shown in the diagram, the efficiency of the acetaminophen removal process was increased by iron oxide-magnetized

bentonite nanocomposite at pH= 4 in concentrations of 25 to 75 mg/l. At pH=4 where a lower adsorbent concentration was needed compared to the other two pHs. Therefore, it can be concluded that the absorption rate of acetaminophen is increased by decreasing pH. This resulted from the protonation of the adsorbent surface and the positive charge of the adsorbent surface. Since the point of zero charge (pH zpc) was 5.22 for the iron oxide-magnetized bentonite nanocomposite adsorbent and pH= 4 was lower than the point of zero charge (pH zpc) of the adsorbent, the surface of the adsorbent had a positive electric charge. On the other hand, pH =4 was lower than the pKa of acetaminophen (9.71), so acetaminophen was present in the cationic form in the solution. Therefore, acetaminophen absorption does not occur on the adsorbent. In conditions where the pH of the solution is acidic (pH < pH zpc), OH ions from the ionic dissociation of water molecules compete with acetaminophen for absorption on the adsorbent surface. As a result, the electric charge of the adsorbent surface becomes negative with the absorption of OH groups and the attraction occurs between acetaminophen cations and hydroxyl groups of acetaminophen [9] on the adsorbent surface of iron oxide-magnetized bentonite nanocomposite by increasing the electrostatic force. Reducing the initial pH of the solution has a direct effect on the surface charge of the adsorbent and changes the chemical state of the pollutant. Therefore, it affects the absorption efficiency.

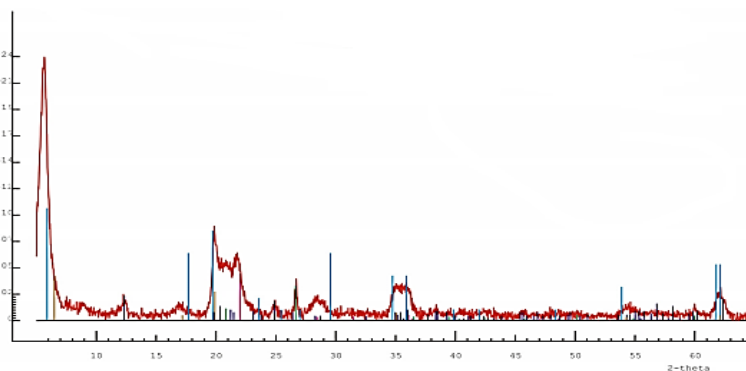


Figure 3. XRD analysis of iron oxide-magnetized nanocomposite.

The effect of the amount of iron oxide magnetized bentonite nanocomposite adsorbent on acetaminophen removal

The effect of the amount of iron oxide-magnetized bentonite nanocomposite adsorbent was investigated as one of the effective parameters in the removal of acetaminophen. The results showed that increasing the amount of adsorbent led to an increase in the removal efficiency of acetaminophen because, with the increase in the amount of adsorbent, the empty and active sites increased. As a

result, a large surface area was provided to the nanocomposite to remove acetaminophen. Although increasing the amount of adsorbent increases the efficiency of pollutant removal, the amount of porosity and pores (active sites) is decreased and the amount of absorption is also decreased per mass unit of the adsorbent due to the unsaturation of some active points on the adsorbent, the special surface with high reactivity of the iron oxide- magnetized bentonite nanocomposite adsorbent [10; 11] and its tendency to become lumpy. Therefore, it can be concluded that increasing the concentration of adsorbent leads to an increase in removal efficiency in terms of percentage from 60 to 100% at pH= 4, reaction time of 30 min, acetaminophen concentration of 25 mg/L in g/dL from 0.5 to 1.

Conclusion

The removal of the drug acetaminophen was investigated in this research using iron oxide-magnetized bentonite nanocomposite and the effects of parameters such as pH, reaction time, the amount of iron oxide-magnetized bentonite nanocomposite adsorbent and the initial concentration of acetaminophen were investigated. The following results were obtained:

- The complete removal of acetaminophen was performed by iron oxide-magnetized bentonite nanocomposite in reaction time of less than 30 min, pH=4, initial acetaminophen concentration of 25 mg/L and adsorbent concentration of 1 g/dL.
- The efficiency of acetaminophen removal in water using iron oxide-magnetized bentonite nanocomposite is greater than bentonite and magnetite nanoparticle reactors.
- The removal of acetaminophen with iron oxide-magnetized bentonite nanocomposite has a greater synergistic effect than the reactors of bentonite and magnetite nanoparticles.
- Increasing the concentration of iron oxide-magnetized bentonite nanocomposite adsorbent, reducing pH and reducing the concentration of acetaminophen lead to an increase in the removal efficiency of acetaminophen.

Disclosure statement and funding

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