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Cu@KF/Clinoptilolite NPs Promoted Removing Cefixime as Antibiotic and 4-nitrophenole as Pollutant from Aqueous Environment

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Abstract

In this work, Cu@KF/Clinoptilolite NPs was synthesized using *Petasites hybridus* rhizome water extract as a simple and efficient green procedure. The obtained catalysts were characterized by XRD, SEM, EDX and TEM analysis. The average particle size diameter of the Cu@KF/Clinoptilolite nanoparticles was approximately 30 nm. The adsorption properties of Cu@KF/Clinoptilolite NPs for the removal of cefixime and 4-NP (4-nitrophenol) from aqueous environment were investigated. Using *Petasits hybridus* leaves water extract, high performance Cu@KF/Clinoptilolite nanoparticles were created in this study. They were then used in numerous reactions to demonstrate the reusability of the nanocatalyst and serve as an environmentally friendly adsorbent for the removal of cefixime (CFX). Also, the catalytic activity of the green synthesized Cu/KF/CP NPs was evaluated in the reduction of organic pollutants such as 4-NP in water at mild conditions. The results indicated that the biosynthesized NCs have very high and effective catalytic activity for organic pollutants within a short time. Some benefits of this process are the quick reaction time, high product yields, and simplicity of catalyst and product separation.

Keywords: Cu@KF/Clinoptilolite NPs; 4-nitrophenol (4-NP); *Petasits hybridus* leaves water extract; Cefixime (CFX).

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Introduction

Dyes and pigments have many uses in the textile, cosmetic, printing, drug, and food synthesis processing. The annual production of dyes and pigments is about ~7 × 10^5 tons per year and most of them are harmful to aquatic organisms [1]. Thus, we require expanded green and eco-friendly methods for the removal of these pollutants from the environment due to their toxicity and carcinogenic properties. Several chemical and physical procedures are reported in the literature for dye behavior including effluents [2]. Although some of disadvantage of these methods are expensive, harmful by-products production and requirements to severe energy. So, green procedures or chemical products are needed for elimination or reduction of these problems.

4-Nitrophenol (4-NP) is a phenol compound and is used in different industries. Nitrophenol is one of the most obstinate compounds owing to their elevated stability and solubility in wastewater content. 4-NP is mostly used to manufacturing of drugs, fungicides, insecticides, synthetic dyes, darken leather, and used in petrochemical plants and textile industries. 4-NP can enter into body through skin or inhalation and passes into the blood stream. Once after inside it is biotransformed into toxic species, which causes several adverse effects. Acute inhalation or intake of 4-NP can cause symptoms such as headaches, drowsiness, nausea and cyanosis in lips, ears, and finger nails. And also, contact with eyes causes exasperation to the humans [1, 2].

Also, water contamination of antibiotic residues, primarily from veterinary and human medications, is a problem [3, 4]. About 30–90% of the medicine administered remains in the body of a person or an animal, and it is frequently rejected as an active agent [5, 6]. The treatment for bacterial infections with multiple medication resistance looks to be challenging, expensive, and ultimately ineffective [7-11], it is vital to understand the symptoms of these illnesses. Prevention is often considered a medical procedure because the use of antibiotics is not limited to a clinical setting. Agriculture and farming use at least half of all pesticides [12]. Therefore, the removal of antibiotic deposits from the environment is important and serves as an interesting case study [13–15]. Cefixime (CFX) is an antibiotic that is a member of the cephalosporin family. Numerous illnesses [16] brought on by bacteria like Staphylococcus ureaus, Streptococcus pneumonia, Escherichia coli, and others are commonly treated with it [17]. As an organic pollutant, the maximum CFX pollution level in water resources is 5 $\mu g\ L^{-1}$. Because of the high use of cefixime as antibiotic in the different diseases in humans and animals, it has a significant position in environmental pollution and maybe cause to stability of pathogenic bacteria in the environment even at low concentrations [18]. Absorption can be particularly helpful in removing pollutants from water or wastewater, even at very low concentrations (less than 1 mg/L). Only a small number of studies [19–22] have examined the removal of antibiotics from wastewater using different sorbents. These active antibiotic are found in the environment (surface water and soil) as a result of excess of domestic, agricultural, and industrial effluents. Some of the commonly used antibiotics were found to be persistent with long half-lives. Thus, they potentially pose adverse effects to water quality and aquatic life. Widespread use of antibiotics alters microbial ecosystems and exerts selective pressure on susceptible bacteria and led to the survival of resistant strains and increase of antimicrobial resistance, making existing antibiotics ineffective in curing various newly emerging infectious diseases. In recent years, antibiotics could trigger allergic reactions in certain individuals and disrupt the native microbial system when they access the human body via the food chain and drinking water. Conventional processes may not eliminate enough amounts of antibiotics from water and wastewater [23]. For this reason, different procedures have been successfully employed for suitable elimination of these pollutants from aqueous solutions involving advanced oxidation processes, electrochemical methods, membrane filtration and adsorption technologies [24-34]. Also, in the present research, *Petasites hybridus* rhizome water extract was studied for the preparation of Cu@KF/Clinoptilolite NPs and used as unique adsorbent for the elimination of CFX and 4-NP from water.

Experimental

General

All materials employed in this work were purchased from Fluka and Merck with no further purification. Antibiotic used in this experiment (cefixime) was obtained from an antibiotic factory located in Sari, Mazandaran, Iran. Antibiotic Factory located in Iran-Sari city. All solutions were prepared in distilled water. The Holland Philips XL30 microscope was used for giving scanning electron microscopy (SEM) image determination of Cu@KF/CP NPs morphology. A Holland Philips Xpert X-ray powder diffractometer, with CuK$_\alpha$ radiation (λ=0.15406 nm) and 2θ ranging from 20 to 80°, was employed for X-ray diffraction (XRD) analysis at room temperature and characterization of crystal structure of Cu@KF/CP NPs. Scherrer's formula; $D= 0.9\lambda/\beta \cos\theta$ was employed for calculating the average crystallite size where D is the diameter of the nanoparticles, λ (CuK$_\alpha$) =1.5406 Å and β is the full-width at half-maximum of the diffraction lines. X-ray energy dispersive spectroscopy analysis (EDS) (S3700N) was utilized for chemical analysis of prepared nanostructures. The shape and size of

Cu@KF/CP NPs were identified by transmission electron microscope (TEM) using a Philips EM208 microscope operating at an accelerating voltage of 90 kV.

Preparation of Cu@/KF/Clinoptilolite NPs [35]

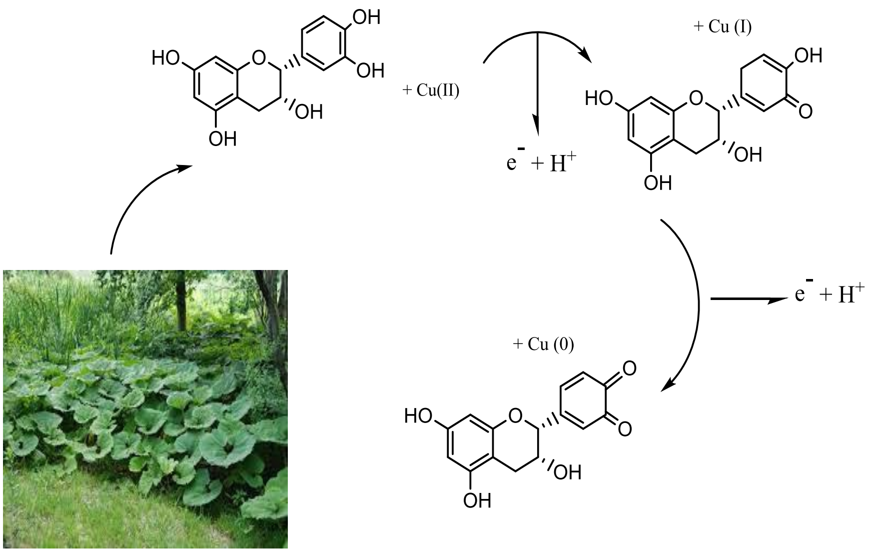
In order to produce nano-sized clinoptilolite, the zeolite was grinded by a zirconia ball mill under dry conditions for 3×20 min. Then, the KF (1 g), 20 mL of 0.05 M $CuCl_2$ solution and 9.0 g nano clinoptilolite was mixed in *Petasites hybridus* rhizome water extract (50 mL) at 100 ^oC in bottom flask for 5 h. Then it was cooled to room temperature, sonicated for 30 min and centrifuged at 7000 rpm for about 10 min for removing the unwanted organic materials and then were filtered. After completion of reaction, water (5 mL) was poured in the mixture.The precipitate was collected by filtration and washed with distilled water and ethanol (96%) for several times. The samples were then heated at 100 °C for 1 h. Produced Cu@KF/CP NPs were dried in the air at room temperature during 24 h.

Catalytic performance of the Cu@KF/Clinoptilolite NPs in organic pollutants such as 4-NP reduction

Typically, 4-Nitrophenol solution (25 mL, 0.0025 M) and Cu@KF/Clinoptilolite NPs (0.005 g) were stirred in a beaker and the mixture was kept at room temperature for 2 min. At this time, the newly prepared $NaBH_4$ (25 mL, 0.25 M) was added beaker for starting the reaction. After adding the aqueous $NaBH_4$, the solution color changed from pale yellow to lemon-colored immediately. The mixture was stirred until the mixture color became colorless. After discoloration of the reaction mixture, 1 mL of the solution was diluted to 25 mL for further UV-vis absorption analysis at certain times. Variations of 4-Nitrophenol concentration were monitored by the UV-vis absorption spectra in the scanning range of 200-700 nm at room temperature. For the confirmation the catalyst reusability, the catalyst was collected by filtration, washed with ethanol, dried and then reused.

Result and disscusion

During this work, we report the ‘‘green-chemical” synthesis of Cu NPs by the reduction of Cu^{+2} ions using *Petasites hybridus* rhizome aqueous extract. The adopted methodology was totally clean, nontoxic and environment friendly. In this work, the Cu metal ions were reduced to nano zero valent (NZV) metallic particles by flavonoid and phenolics present in the extract of *Petasites hybridus* rhizome according to the below mechanism (Scheme 1).



Scheme 1. Mechanism of synthesized Cu NPs using the aqueous extract of *Petasites hybridus* rhizome.

The progress of the reaction between metal ions and aqueous extract of *Petasites hybridus* rhizome to produce the Cu NPs was monitored by recording the absorption spectra as a function of time which demonstrated the formation of Cu NPs after 10 min indicated the typical surface resonance band of Cu nanoparticles from 550 to 600 nm (Figure 1). Furthermore, the stability of Cu NPs was monitored by UV–vis spectroscopy at 48 h min to 15 days which shows that even after 15 days the prepared Cu NPs employing this procedure are extremely stable with no significant variance in the spectra, position and symmetry of the absorption peak.

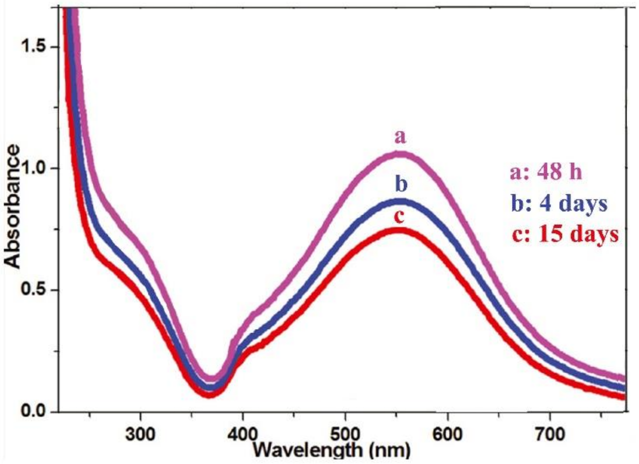


Figure 1. UV–vis spectrum of the Cu NPs.

Catalytic performance of the Cu@KF/CP NPs in 4-NP reduction

In this work, 4-nitrophenol was chosen for study of the catalytic activity of the synthesized Cu@KF/CP NPs in water at ambient temperature. The dye reduction processes were checked by recording the variations in the UV–Vis absorption spectrum of the reaction mixture at room temperature, which was made free from the catalyst by centrifugation.

Initially, we chose to study the reduction of 4-nitrophenol to 4-aminophenol (4-AP) as the model reaction in the presence of Cu@KF/CP NPs. The experiments control without catalyst in the presence of $NaBH_4$ did not show any appreciable conversion. This result clearly demonstrates that the Cu@KF/CP NPs is necessary for the reduction of 4-nitrophenol to 4-aminophenol. This conversion was monitored by using UV–Vis measurements and the results shown in Figure 7. 4-nitrophenol in aqueous medium showed the absorption at 317 nm. However, there was a red shift of the peak of 4-nitrophenol from 317 to 400 nm (due to the generation of 4-nitrophenolate ion), observed immediately after the addition of prepared aqueous solution of $NaBH_4$, corresponding to a significant change in solution color from light yellow to bright yellow. In the absence of the Cu@KF/CP NPs, the peak at 400 nm remained unaltered even after 15 h, indicating the inability of the strong reducing agent $NaBH_4$ alone which reduced 4-nitrophenolate ion even though the reaction medium contains the electron donor (BH_4^-) and proton source (H_2O). In addition, when the Cu@KF/CP NPs was added into the 4-nitrophenol solution solely without $NaBH_4$, the absorbance of 4-nitrophenol solution remained unaltered for several hours. In the presence of the Cu@KF/CP NPs and $NaBH_4$, the absorbance at 400 nm decreased to about zero rapidly within 5 min; meanwhile, a new peak at about 300 nm which was ascribed to 4-aminophenol appeared and gradually increased with the bleaching of the yellow color of the reaction solution (Table 1).

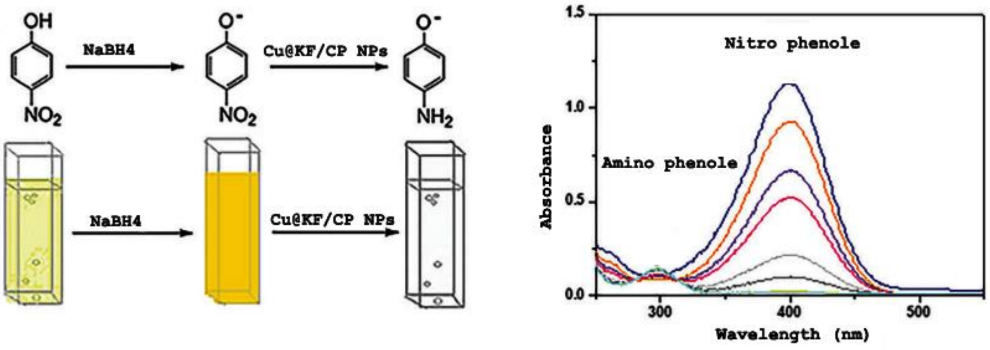


Figure 2. UV–Vis spectrum of reduction of 4-nitrophenol.

For a reduction reaction, the effects of the catalyst and $NaBH_4$ quantity were determined. As shown in (Table 1, entry 1), no reaction was produced in the absence of the catalyst. So, this proves that the catalyst's surface is where catalytic reduction takes place. At room temperature, 25 mL of $NaBH_4$ 0.3 M and 0.005 g of catalyst produced the best results (Table 1, entry 5). A general glance at Table 1 revealed that the catalytic performance improved with an increase in the NaBH4 concentration. The complete conversion was attained in 295 seconds in the presence of (25 mL, 0.3 M) of the $NaBH_4$ and 0.005 g of catalyst.

Table 1. Catalytic reductin of 4-NP using Cu/KF/CP NPs and $NaBH_4$.

Entry	**Catalyst (g)**	**$NaBH_4$ (Mol/Lit)**	**Time (s)**
1	0	0.15	24 h[a]
2	0.005	0.15	460
3	0.005	0.25	420
4	0.005	0.3	380
5	**0.005**	**0.3**	**295**
6	0.007	0.3	295

[a] no reaction without the catalyst

The structure of the synthesized Cu@KF/CP NPs was confirmed using SEM, XRD, EDX, and TEM images. In the study of nanomaterials, field emission scanning electron microscopy (FESEM) is a secondary electron detection method used in conjunction with a field emission source to produce high-resolution surface imaging. In this process, a strong electric field causes the release of electrons from a conductor's surface. Figure 3 depicts the surface morphology of Cu@KF/CP NPs as determined by the FESEM approach.

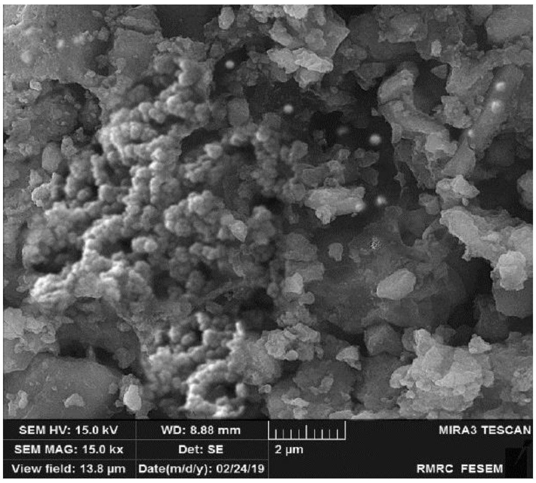


Figure 3. SEM representation of Cu@KF/CP NPs.

Unknown nanoparticles' small crystalline regions can have their size, shape, and internal tension determined using a nondestructive technique called X-ray diffraction examination. Figure 4 depicts the Cu@KF/CP NPs' X-ray diffraction spectrum. According to the Debye-Scherrer equation, the average crystallite size of Cu@KF/CP NPs was approximately 30 nm. For the prepared Cu@KF/CP NPs the peaks observed at 2θ values of 43.39^{o}, 50.49^{o} and 74.18^{o} correspond to (111), (200) and (220) planes of metallic Cu. These three peaks were quite consistent with those of the standard JCPDS Card No. 04-0836 for the standard spectrum of the pure fcc (face centered cubic) metallic Cu. The peaks appear at $\sim 18.2^{o}$ (111), 19.9^{o} (110), 21.8^{o}(100), 21.9^{o} (200), 26.7^{o} (101), 29.9^{o} (220), 34.5^{o} (121), 36.8^{o} (222), 41.5^{o} (400), 50.0^{o} (112), 53.0^{o} (422), 62.1^{o} (440) which are indexed to (220), (311), (400), (511) and (440) planes which correspond to the crystal structure of KF/CP nanoparticles and the observed peaks are well matched with the JCPDS card no. 39-1383.

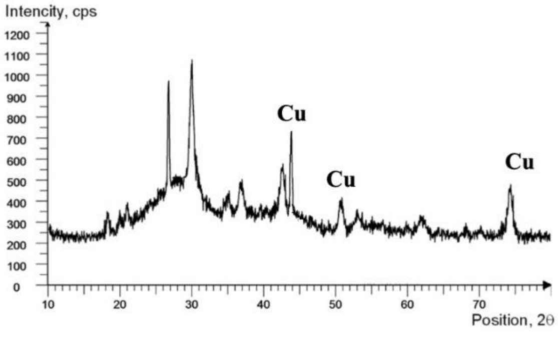


Figure 4. X-ray diffraction spectra of Cu@KF/CP NPs.

By using the EDX method, the elements in the greenly synthesized Cu@KF/CP NPs were analyzed (Figure 5). As seen in Figure 4, observing the C, Cu, K, and F peaks of NPs proved that Cu@KF/CP NPs were successfully synthesized. Also indicating the existence of organic molecules at the nanoscale is the peak carbon in the EDS spectrum. The absence of an impurity peak in the EDX spectra demonstrates the uniform distribution of constituent elements and verifies the cleanliness of the processed samples.

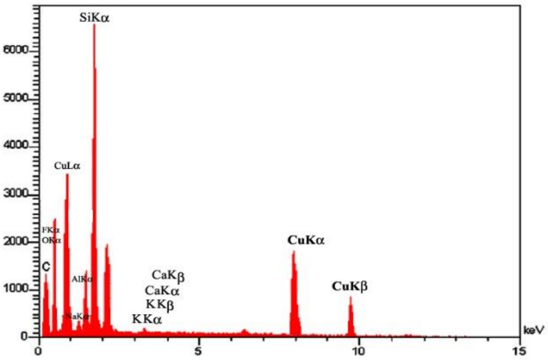


Figure 5. EDX image of green Cu@KF/CP NPs.

The excellent quality and apparent size, form, and structural image of the Cu@KF/CP NPs are obtained using the transmission electron microscopy (TEM) examination (Figure 6). The Cu@KF/CP NPs that were produced were fewer than 35 nm in size, according to the TEM picture.

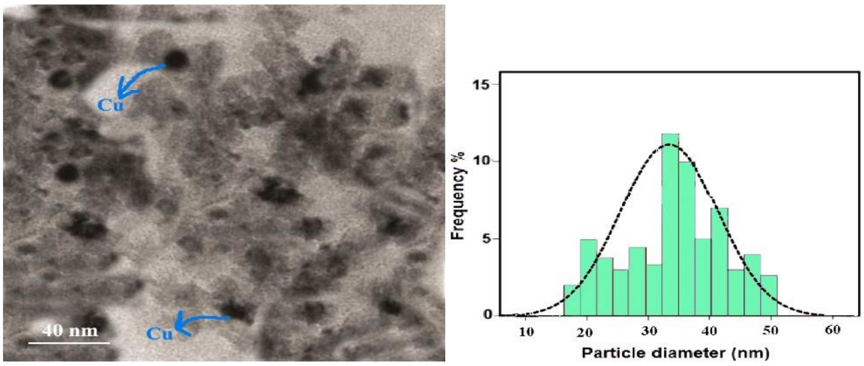


Figure 6. TEM image of the Cu@KF/CP NPs.

Brunauer–Emmett–Teller (BET) adsorption isotherm analysis

By analyzing the adsorption isotherms of nitrogen on the surface of the Cu@KF/CP NPs at increasing relative pressure, the BET surface area, pore size and volume were determined (Figure7).

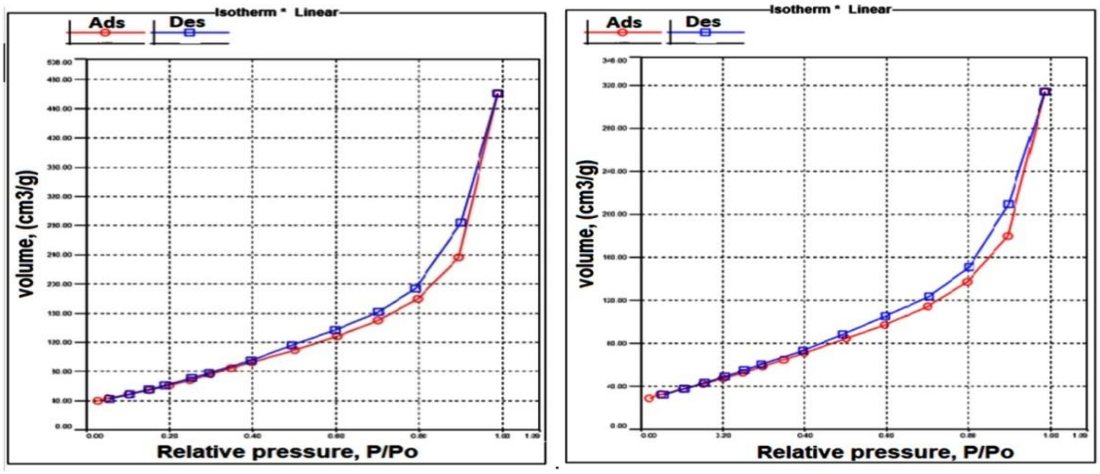


Figure 7. Adsorption and Desorption isotherm of KF/CP (left) and Cu/KF/CP nanocomposites (right).

The surface areas of Cu@KF/CP NPs have been commonly characterized using the BET method based on adsorption isotherms of unreactive nitrogen. The BET analysis confirmed the surface areas that display improvement the Cu@KF/CP NPs surface using a decrease in the measurable surface area of the Cu@KF/CP NPs nanoparticles. As shown in Table 2, the surface area (S), mean diameter (R) and volume pore size (V) of the adsorbents have changed and the BET surface area of KF/CP NPs pores decreased from 262.3 to 201.8 m^2/g.

Table 2. N_2 adsorption-desorption data of KF/CP NPs and Cu@KF/CP NPs.

Adsorbant	**S $_{BET}$, m^2/g**	**V $_{total}$, cm^3/g**	**R, nm**
KF/CP NPs	262.3	0.714	10.6
Cu@KF/CP NPs	201.8	0.486	9.54

Application of Cu@KF/CP NPs in the adsorption of Cefixime

In continuous procedure, Cu@KF/CP NPs as adsorbent and cefixime were poured in the pot and stirred at a certain time until the adsorption process was performed. For this reason, by performing the adsorption experiment in several pHs, the best amount of pH that the adsorption is maximum was selected. Then, the contact time, the amounts of adsorbent and the initial concentration of cefixime were investigated. The amount of cefixime in this research was 1000 mg.L^{-1}. The experimental solutions were prepared by diluting the standard solution with deionized water. After completing the experiment, the liquid and solid phases were separated and the cefixime concentration was measured. For the separation of catalysts, we are using the external magnet. All the experiments were performed in triplicate, and the mean values have been used in calculations. In any adsorption experiment, was measured equilibrium adsorption capacity (qe) and R%. The equilibrium adsorption capacity (qe) is the amount of adsorption cefixime for 1 g adsorbent in equilibrium time.

$$q_e = \frac{(C_o - C_e)V}{W} \qquad R = \frac{C_o - C_e}{C_o} \times 100$$

That C_0 and C_e are initial concentration and equilibrium concentration of cefixime respectively and V is the volume of cefixime (L) and W is the amount of adsorbent (g).

$$q_e = \frac{(C_o - C_e)V}{W} \qquad R = \frac{C_o - C_e}{C_o} \times 100$$

Investigation the Factors affecting adsorption

Effect of pH

In this research, another purpose after synthesis of Cu@KF/CP NPs is an evaluation of the ability of this nanocomposite for the adsorption of cefixime. The several factors are important for adsorbing of cefixime by Cu@KF/CP NPs. The pH has a very important role in the adsorption of cefixime by Cu@KF/CP NPs by affecting the charge transfer on the adsorbent interface. The pH effect is investigated in the range 2–10 on the removal of cefixime with the initial concentration of 10 $\mathrm{mg.L^{-1}}$ of cefixime (Figure 8). The efficiency of cefixime removal increases with decreasing pH values.

The maximum amount of cefixime being adsorbed on the surface of Cu@KF/CP NPs at pH=2.The experimental results of adsorption by Cu@KF/CP NPs in various pH exhibited that while pH=10, a sharp decline in adsorption of cefixime took place.

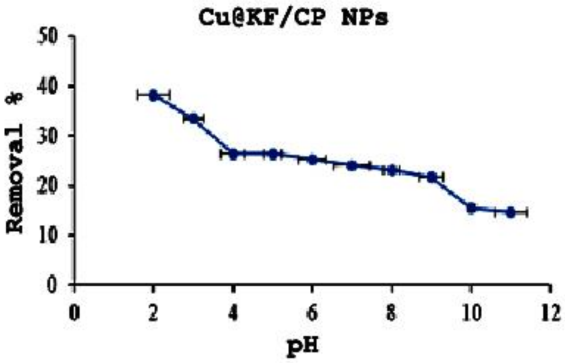


Figure 8. Effect of pH on the removal of cefixime (10 mg.L^{-1}) in 47 min, Cu@KF/CP NPs (30 mg) in wastewater (100 mL).

The contact time effect

The time effect of contact between sorbent and cefixime was shown in Figure 9. It is clear that a significant enhancement was seen in the adsorption ability of cefixime. Firstly, the adsorption rate is very fast because cefixime from 10 to 50 minutes might be effectively adsorbed on the outside surface of Cu@KF/CP NPs. Then the slope of adsorption enhancement is mild and in the equilibrium time became constant.

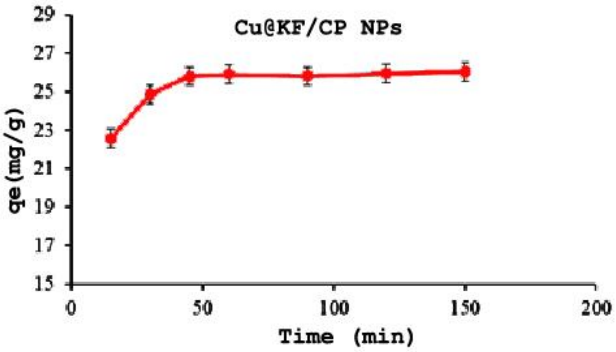


Figure 9. Time of contact effect on adsorption of cefixime (10 mg.L^{-1}) in pH=2, Cu@KF/CP NPs (30 mg) in wastewater (100 mL).

The amounts of adsorbent effect

A variety of adsorbent quantities have been utilized to remove cefixime in order to reach the optimized circumstances. As seen in Figure 10, the amount of cefixime adsorption increased as adsorbent quantities were raised. As a result, 30 mg of Cu@KF/CP NPs were obtained as the optimal dosage for the elimination of cefixime.

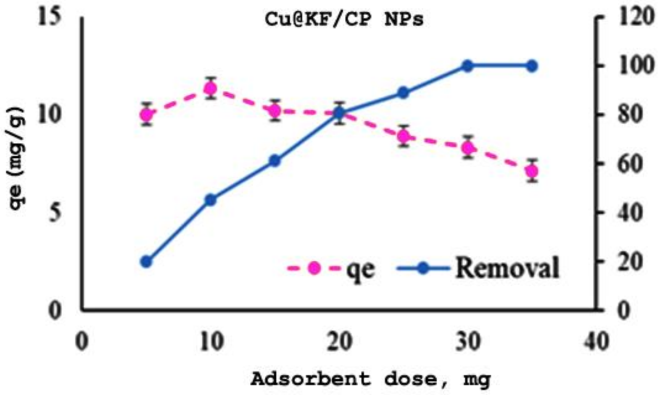


Figure 10. Effect of Cu@KF/CP NPs amounts on adsorption of cefixime.

Adsorption isotherms

The capacity of Cu@KF/CP NPs as a cefixime adsorbent is extensively revealed by the equilibrium analysis on the cefixime adsorption. An adsorption isotherm with specific constant quantities shows the surface characteristics and dependence of the Cu@KF/CP NPs. It can also be utilized to compare the Cu@KF/CP NPs' ability to act as an adsorbent for various contaminants. In this study, cefixime adsorption was investigated using the Langmuir, Freundlich, Redlich-Peterson, and Dubinin-Radushkevich isotherms. The maximum adsorption capacity of Langmuir isotherm was obtained 54.05 mg/g for the adsorption of cefixime by Cu@KF/CP NPs as adsorbent that the appropriate amounts of Cu@KF/CP NPs exhibited the linear regression (Figure 12). Also, Redlich-Peterson isotherm was used for determination of the exact matching of the adsorption process with Langmuir and Freundlich that it is a combination of both Langmuir and Freundlich models. In this model, it is assumed that when $\alpha \sim 0$, the data is matched with the Freundlich model better than Langmuir but when $\alpha \sim 1$, the results will match with the Langmuir model. As shown in Figure 12, $\alpha = 0.87$ for Cu@KF/CP NPs. Accordingly, the absorption of the cefixime by the synthesized Cu@KF/CP NPs as adsorbent shows the uniform absorption of the single layered. The Dubinin-Radushkevich model was used to calculate energy and the type of adsorption (Figure 12). If the value of E = 8-16 kJ/mol, the adsorption process carried out by chemical ion-exchange and if E <8 kJ/mol the adsorption process is physical, whereas if the value is more than 16 kJ/mol, the adsorption process is chemisorptions. The rate constant values for Dubinin and

Radushkevich isotherm shown that E-value was lower than 8 kJ/mol that confirmed the cefixime adsorption by Cu@KF/CP NPs is physical sorption.

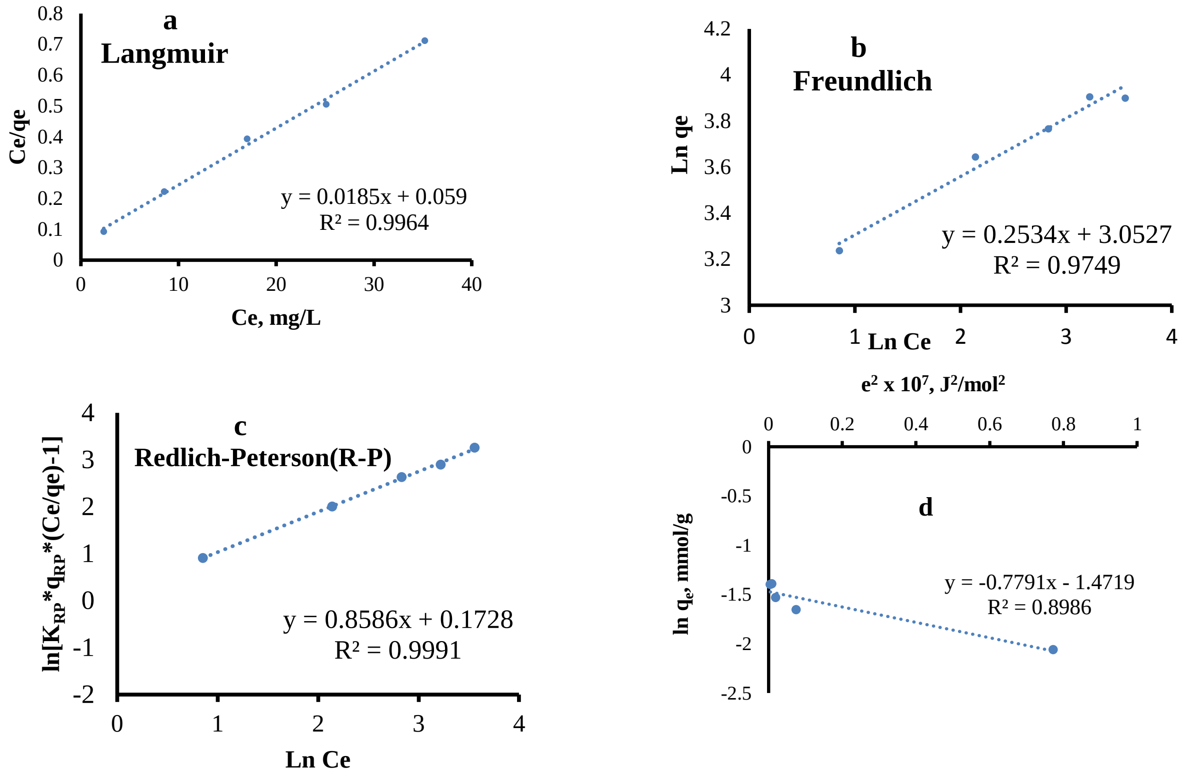


Figure 11. Determined isotherm model curves for the adsorption of cefixime on Cu@KF/CP NPs.

Conclusion

In this study, the Cu@KF/CP NPs as a new heterogeneous nanocatalyst were prepared via a simple method and characterized using XRD, FESEM, EDX and TEM analyses. The catalytic performance was also considered for reduction of variety of dyes in water. The advantages of this procedure are easy and green preparation of catalyst, high performance of catalyst in removal of cefixime, easy separation of adsorbent, high efficiency and reusability of it. We could used new mixed metal oxide and nutrolite as zeolite instead of clinoptilolite.

Acknowledgments

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