Novel Fibrous Silica-Copper Sulfide Nanocomposite (KCC1-CuS): Synthesis and Enhanced Photocatalytic Degradation of Humic Acid

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Research Article

Keywords: Humic acid, Photocatalytic degradation, Fibrous silica-copper sulfide nanocomposite

Posted Date: February 22nd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-157129/v1>

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Novel fibrous silica-copper sulfide nanocomposite (KCC1-CuS): synthesis and enhanced photocatalytic degradation of humic acid

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Abstract

The present study aims to test the degradation ability of KCC-1/CuS nanocomposite as a new photocatalyst for Humic acid (HA) degradation. The degradation process was accomplished using a photocatalytic reaction under irradiation by UV light. Structural characteristics of synthesized nanoparticles were done using Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDX). Furthermore, the effect of important degradation variables such as pH (3–11), nanocatalyst dosage (0.005-0.1 g/L), HA concentration (2–15 mg/L), and contact time (0–90 min) were investigated. SEM and TEM images showed that the size of KCC-1/CuS nanocomposite was approximately 50 nm. According to the results of the study, the maximum degradation of HA was 89.5% in the photocatalytic degradation process of HA by KCC-1/CuS nanocomposite under UV light at the optimum condition of pH = 3, nanocomposite dose of 0.1 g/L, HA concentration of 2 mg/L and contact time of 90 min.

Key Words: Humic acid, Photocatalytic degradation, Fibrous silica-copper sulfide nanocomposite

1. Introduction

The problem of water pollution is a major environmental issue. In recent years many pollutants enter the water as a result of urbanization and industrialization, and as a result, worldwide attention has been focused on controlling water pollution (Reddy & Lee 2013). Water resources worldwide contain natural organic matter (NOM) resulting from the interaction between the geosphere, hydrosphere, and biosphere (Murray & Parsons 2004). The presence of humic acid as a NOM in water resources could be affect water quality by increasing coagulants and disinfectants, and producing complex material in distribution systems, as well as providing a basis for the production of disinfection by-products (Kabsch-Korbutowicz et al. 2008). Humic acid consists of two hydrophobic and hydrophilic parts, and contains functional groups such as -C=O, -COOH, and -

OH related to the aliphatic and aromatic part of the molecule (Nghah et al. 2011). Humic substances make up 50-80% of the organic matter in soil and water, and made up of carbon, hydrogen, oxygen, nitrogen, and sometimes sulfur (Jones & Bryan 1998). As the concentration of humic acid in the aquatic environment increases, it changes the properties of water such as odor, taste, and color (Liu et al. 2016). Humic acid molecules can bind strongly to heavy metals and synthetic organic matter, making it difficult to remove contaminants from the water (Li et al. 2011). Also, reaction of HA with chlorine in drinking water intensifies the production of carcinogenic by-products (Bolto et al. 2004). Although HA compounds are not carcinogenic by themselves, they produce secondary problems during the process of purifying drinking water, including changing taste, color, and odor (Fearing et al. 2004), adverse effects on membrane function (Fan et al. 2002), corrosion of metal facilities (Yoon & Lueptow 2005), re-growth of microorganisms in the water supply system and water storage tanks (Panyapinyopol et al. 2005), and increase the use of disinfectants in water treatment. During the disinfection process, HA compounds can react with disinfectants and create more than 600 types of disinfectant by-products, such as haloacetic acids and trihalomethanes, which can cause cancers including colon cancer and bladder cancer (Matilainen et al. 2010). The removal of HA in drinking water is carried out by various processes, including adsorption, coagulation, advanced oxidation, membrane processes, ion exchange, chitosan polymers (Doulia et al. 2009), and photocatalysis (Liu et al. 2008). In many areas of the world, before chlorination, HA is removed by various processes, including coagulation followed by filtration. Although the coagulation process eliminates HA, it creates many underlying problems, including high sludge production with alum as well as high operation cost (Mesdaghinia et al. 2006). Among these methods, the advanced oxidation process appears to be more suitable for the treatment of waters containing NOM (Yang & McGarrah 2005).

In the last decade, advanced oxidation processes as a suitable high-performance method for HA elimination have been the focus of many researchers. The methods used in advanced oxidation processes include ultrasound, electro-Fenton, photo-Fenton, ozonation, UV/ozone, electro/persulfate, ultrasonic/persulfate, photocatalytic, etc. The benefits of these processes include the production of free radicals with high oxidation potential, high efficiency in breaking down organic matter, low start-up costs, and variability in methods (Hou et al. 2013, Kang et al. 2016). Photocatalytic purification of various pollutants by use of radiation in the presence of a suitable photocatalyst can damage and degrade the pollutants and transform them into safe by-products as well as reduce the purification steps. The mechanism of the photocatalytic process involves the irradiation of ultraviolet light to the semiconductor material and subsequent electron excitation from the valence band to the conduction band, and this electron excitation produces hydroxyl radical in aqueous solutions (KordMostafapour et al. 2016). Various semiconductor materials have been used to investigate the photocatalytic properties, including metal oxides and metal sulfides such as (Asgari et al. 2011) CuS (Isac et al. 2019) CdS (Zhang et al. 2019) WO₃ (Liu et al. 2019) ZnO, (Oskoei et al. 2016) TiO₂ (Schneider et al. 2014). Copper sulfide (CuS) is a semiconductor that is non-toxic, inexpensive, accessible, and sustainable in the environment. Copper sulfide with 2.0 V band gap is also an important semiconductor material which is very effective in terms of physical, chemical, electrical, magnetic properties. In recent years, materials with organic-metal bonds such as CuS, have received considerable attention due to their high photocatalytic potential in the presence of ultraviolet radiation to remove organic compounds from aquatic environments. Fibrous silica KAUST Catalysis Centre KCC-1 has a unique fiber morphology and also a high level of thermal and mechanical stability so it offers excellent execution in contrast with different sorts of silica, making it ideal for use as sorbent applications (Polshettiwar et al. 2010). It has been successfully used in a variety of applications, such as CO₂

capture, photocatalysis, DNA and gene transfer, hydrogenesis reactions, and hydrothermal reactions (Fihri et al. 2012, Huang et al. 2014).

In this study, KCC-1/CuS nanocomposite was synthesized for the first time and used for HA degradation from aqueous solutions. To improve the efficiency of the nanocomposite in pollutant degradation, parameters such as solution pH, contact time, nanoparticle dose, and HA concentration were studied.

2. Materials and Methods

2.1 Chemicals

The chemicals used in this study to synthesize the KCC-1/CuS nanoparticles were cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$), urea (CH_4N_2O), tetraethyl orthosilicate, TEOS ($SiC_8H_{20}O_4$), cyclohexane (C_6H_{12}), 1-pentanol ($C_5H_{12}O$), ethanol (C_2H_5OH), Copper(II) sulfate ($CuSO_4$), ethylene glycol ($C_2H_6O_2$), and sodium thiosulfate ($Na_2S_2O_3$). All chemicals were purchased from Merck Co. (Germany) and were used without further purification.

2.2 KCC-1/CuS synthesis and characterization

2.2.1 Synthesis of KCC-1 nanoparticles

To synthesis of KCC-1 nanoparticles, 2.0 g of triethylmethyl ammonium bromide and 2.4 g of urea were dissolved in 100 ml of water and was placed on a mixer for 15 minutes. Then 10 ml of TEOS was mixed with 10 ml of cyclohexane. This solution was added dropwise to the previous solution and placed on the stirrer again for 15 minutes. After that, 6 ml of 1-panthenol was added to the solution and was placed at room temperature on the stirrer for 20 minutes. It was then placed in an oven at 120 °C for 1 h and was allowed to settle at room temperature (Dhiman et al. 2015).

2.2.2 Synthesis of KCC-1/CuS nanocomposite

Copper sulfate was used to modify the surface of KCC-1 nanoparticles. First, 0.15 g amount of KCC-1 nanoparticles was dispersed in ethylene glycol solvent (120 °C), and copper sulfate was

added to it. After dissolving the copper sulfate in the above solution, the sodium thiosulfate solution was added, and the reaction mixture was refluxed at 90 °C for 90 min. The resulting nanocomposite was then separated by centrifugation, rinsed with deionized water and ethanol several times, and dried in a vacuum oven for 8 hours (Beyki et al. 2016).

2.2.3 Characteristics of the synthesized nanocomposites

Different analysis was utilized to identify the surface morphology and structural characteristics of the synthesized KCC-1/CuS nanocomposite. Transmission electron microscopy (TEM) and field emission-scanning electron (FE-SEM) with high-resolution micrographs were applied to characterize the morphology, size and shape of the nanoparticles. The Fourier transform infrared (FT-IR) analyses were applied to investigate the functional groups. XRD analysis was used to determine the crystalline structure of the components of the sample, while EDS was used to find out the elemental composition of the sample.

2.3 Experiments

According to Scheme 1, the reactor used in this study consists of two parts. The main enclosure (reaction enclosure) where all the testing procedures are carried out. The secondary enclosure, which surrounds the main chamber and reduces the temperature of the UV-C radiation compartment by the continuous flow of water.

The lamp used as a radiation source was UV-C with a power consumption of 18 watts, a generated wavelength of 253.7 nm, a lifespan of 8000 hours and a radiation intensity of $282\text{--}294 \frac{W}{m^2}$. The length of the lamp was 22 cm, which was placed in a quartz sheath with a diameter of 5 cm in the center of the reactor (Scheme 1).

The removal efficiency of HA in the photocatalytic process using KCC-1/CuS nanocomposite was tested as a function of different solution pH values (3, 5, 7, 9, 11), nanocomposite dosage (0.005,

0.01, 0.02, 0.03, 0.04, 0.05, 0.1 g/L), initial HA concentration (2, 5, 7, 10 and 15 mg/L), reaction time (10, 20, 40, 60 and 100 min). All these experiments were conducted using 300 mL flasks and mixing speed of 300 rpm. Before starting the photocatalytic process under UV light, the flasks were on the dark condition for about 30 min to determine the adsorption/desorption equilibrium. After this step the concentration of HA measured using UV spectrophotometer (T80, UV/Visible, United Kingdom) at a spectral peak of 254 nm and considered as initial concentration. After specific times of light radiation, the HA concentration was measured again and considered as secondary concentration. The HA removal efficiency (%R) were determined using the following equation:

$$\%R = ((C_0 - C_t) \times 100) / C_0 \quad (1)$$

Where C_0 and C_t are the measured HA concentrations (mg/L) before photocatalytic process and after specific time of it.

Scheme 1. Schematic representation of the reactor used for the photocatalytic degradation of HA.

3. Results and discussion

3.1 Characterization of KCC-1/CuS samples

The results of the FTIR analysis of KCC-1 and KCC-1/CuS in the range of 500-4000 cm^{-1} were presented in Figure 1. The functional group of Si-O bending, O-H stretching vibration, and Si-O asymmetric stretching were appeared at around 460, 3435, 1055 and 766 cm^{-1} peaks respectively. Also these peaks have been appeared in FTIR spectrum of KCC-1/CuS nanocomposite. The Si-O bending, Si-O symmetric and asymmetric stretching vibrations were indicated by the peaks at 465, 1102, and 796 cm^{-1} , respectively (Yin et al. 2019). The presence of O-H molecules may also be demonstrated by the appearance of 3420 cm^{-1} FTIR peak (Fihri et al. 2012, Huang et al. 2014).

Fig. 1. FTIR spectrums of KCC-1 (a) and KCC-1/CuS (b) nanocomposite

The TEM analysis was carried out to explore the morphology and size of the microspheres. According to Figure 2 the spheres display radial fibrous structures (50 nm). The TEM images show that silica fibers expand from the middle to the outside. A useful indicator of adsorption efficiency is considered to be the surface area and porosity of the microspheres.

Fig.2. TEM images of KCC-1/CuS nanocomposite

The TGA thermogram of KCC-1/CuS NPs is shown in Figure 3 which show the weight loss between 30 °C and 100 °C, which is related to the adsorbed water molecules on the support. The organic group functionalized analogs KCC-1/CuS NPs showed a significant weight loss at ~300 °C, due to ligand decomposition. As shown in Figure 3, a significant weight loss step, which was attributed to the decomposition of material oxidizes, appeared at the temperature range of 300–380 °C. Another small peak at around 600 has been appeared because of oxidaton (Xie &Wosu 2016).

Fig.3. TGA analysis of KCC-1/CuS nanocomposite

The EDS analysis was used to define the elemental composition of KCC-1/CuS NPs, the results are shown in Figure 4. According to the EDX spectrum, it is evident that elements are sort down

by abundance as Si, O, S, Cu. The formation of the KCC-1 as the core of the nanocomposite can be concluded from the presence of Si and O that are detected at 0.5 and 1.7 keV, respectively. In addition, the presence of Cu and S with a high ratio confirms the CuS coating (outer shell) onto KCC-1 particles to form KCC-1/CuS MNC.

Fig.4. EDS results of KCC-1/CuS nanocomposite

As shown in Figure 5 the XRD pattern was performed from 9.0° (2θ) to 79.0° (2θ) to confirm the crystallinity of the synthesized nanocomposite. Also, using this analysis is proportional to obtain more information about the molecular structures of the synthesized nanocomposite. Strong and sharp scattered peaks indicate that the resulting nanocomposite is very crystalline. The two sharp peaks at $2\theta \approx 32^\circ$ and $2\theta \approx 48^\circ$ are related to the crystalline parts. The average crystallite size of KCC-1/CuS was also calculated via XRD analysis using Debye-Scherrer's equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad \text{Eq.2}$$

Where D is the diameter of particles, λ is the wavelength of X-ray radiation ($\lambda=0.154$ nm), β is full width at half maxima (FWHM), and θ is Bragg's angle (Rahimi et al. 2020). The average crystalline size was calculated to be 50 nm, which was further confirmed from TEM.

Fig.5. XRD patterns of 7 KCC-1/CuS NPs

3.2 The impact of solution pH

The solution's pH has a significant effect in the photocatalytic processes, which may affect the cycle of degradation of organic molecules in many ways. The two most significant considerations are the quality of breakdown of polluting molecules and the surface charge of the catalyst used. Accordingly, the surface charging of the catalyst may be examined by evaluating the pH_{pzc} (the point of zero charge) value. In this way, the pH_{pzc} determination study was applied. The pH_{pzc} of KCC-1/CuS NPs is obtained to be 5.3 (Fig.6.a). When the solution pH is greater than 5.3 value,

the surface of nanoparticles would have negative charges resulting from surplus OH^- ions. From another side, when the solution pH is less than 5.3 value, the surface of nanoparticle will be positively charged, producing H^+ protons. HA has both hydrophobic and hydrophilic functional groups such as the carboxyl, phenolic hydroxyl, alcoholic hydroxyl, and carbonyl forms. As shown in Figure 6b the HA degradation efficiency is reduced at alkanoic pHs because of the high repulsion of negatively charged carboxylate ions form of nanocomposite (Wiszniowski et al. 2003). The maximum degradation efficiency of HA equal to 49.5% recorded at pH=3. This is because the surface charge of the catalyst is positive at pHs lower than pH_{zpc} . So the nanocomposite can react more effectively to hydroxyl groups of HA in the solution. The results of another study on efficiency of photocatalytic degradation of humic acid using magnetic nanoparticles (Fe-doped $\text{TiO}_2/\text{Fe}_3\text{O}_4$) showed that the efficiency of humic acid removal increased under acidic conditions and reached its maximum at pH 3, but decreased at basic and neutral pH values (Moein et al. 2020).

Fig.6. a) The pH_{zpc} of KCC-1/CuS nanocomposite b) Effect of pH in photocatalytic degradation of HA by KCC-1/CuS (HA concentration: 15 mg/L, catalyst dosage: 0.03 g/L).

3.3 The impact of Catalyst dose

The effect of catalyst dose on the degradation efficiency of HA in the range of 0.005 to 0.1 g/L was investigated. According to the results shown in Figure 7, increasing the KCC-1/CuS dose leads to increasing the efficiency of HA degradation. The highest decomposition efficiency was observed in the nanocomposite dose of 0.1 g/L, so that the degradation efficiency of 88.6% is achieved in 90 minutes. Increasing the efficiency of photocatalytic removal of HA by increasing the amount of catalyst dose in this study can be explained by increasing the available surface area and the number of active sites at the catalyst surface (to absorb optical photons). Therefore, upon UV irradiation, more electron holes are produced, which leads to an increase in the presence of oxidizing radicals and the degradation of HA. The same results are reported by Eslami et al.(2015) that with increasing the catalyst dosage of N, S co-doped TiO₂ from 0.5 to 2 g/L, the non-steroidal anti-inflammatory ibuprofen degradation increased from 42% to 85% (Eslami et al. 2016).

Fig. 7. Effect of catalyst dosage in photocatalytic degradation of HA by KCC-1/CuS (HA concentration: 2 mg/L, pH=3)

3.4 The impact of HA concentration and contact time

The initial concentration of contaminants is another important factor in the efficiency of UV/ KCC-1/CuS process. In this study, the effect of the HA concentration of 2 - 15 mg/L was investigated on the HA degradation (other parameters were constant at the optimized values of pH=3, catalyst dose of 0.1 g/L), and the results have been shown in Fig 8. Results indicate that increasing the HA concentration from 2 to 15 mg/L led to a reduction in efficiency of the process from 89.5% to 17.3% at a reaction time of 90 min. The reason for a reduction of efficiency with the increase of HA concentration is that in lower concentrations, more active sites on the surface of nano-catalysts are available to adsorb the contaminant. But increasing the concentration of HA led to a decrease in the available surface of the catalyst and increasing the repulsive forces between them. Based on the other aspect, it can be interpreted that at higher HA concentrations, the generation of hydroxyl radicals on the surface of the catalyst reduces since the active sites of the catalyst might be saturated by the pollutant (Gnanaprakasam et al. 2015). In a study of sonophotocatalytic degradation of diazinon using Fe-TiO₂ nanoparticles at various initial concentrations of diazinon in aqueous solutions, Tabasideh et al. concluded that the efficiency of diazinon removal decreased with increasing the concentration of it (Tabasideh et al. 2017). Li et al. obtained a similar finding in an investigation of the photocatalytic degradation of humic acid. They found a noticeable decrease in the removal efficiency with increasing concentrations of contaminants (Li et al. 2002). Reaction time is also an important parameter that affects the process of decomposition of the pollutants regardless of the type of catalyst (homogenous or heterogeneous). So the degradation efficiency of HA was investigated in the range of 0 to 90 min of reaction time at different HA concentrations. According to Figure 8, it is obvious that for HA concentration of 2 mg/L by increasing the reaction time from 0 to 90 min the degradation efficiency increased from 12.0 to 89.5%. Ghasemi et.al; observed similar results by increasing the contact time from 20 to 80 min,

the furfural degradation using UVC/TiO₂/GAC composite decreased, and the irradiation of 80 min was considered as the optimum value.

Fig. 8. Effect of HA concentration in photocatalytic degradation of HA by KCC-1/CuS (catalyst dose: 0.1 g/L, pH=3)

3.5 Mechanism of HA degradation

Semiconductors such as CuS particles have two forms of mobile carriers, including electrons in the conduction band as well as positive holes in the valence band (Arghavan et al. 2020). The bandgap is the space in the middle of the valence and conduction bands, and the energy gap sequesters the bands. As the semiconductor irradiates with more energy than the semiconductor band, these photons will switch the electron energy from the valence band to the conduction band. This process will make an electron cavity within the external shell of CuS. So, a positive hole charge (h^+) and a negative electron (e^-) would produce (eq. 3), which, oxidizes O₂ and H₂O molecules and simultaneously produce highly active $\cdot O_2^-$ and $\cdot OH$ groups (eqs.5 and 6).

If there are no suitable electron-hole scavengers, the produced electron-hole pairs can recombine the input energy as heat (Lei et al. 2021). Organic matter such as HA molecules in the aqueous solution will be degraded and transformed into non-toxic byproducts such as CO₂, H₂O and mineral acids (Eqs 7 to 10).

4. Conclusion

In the current study, KCC-1/CuS nanocomposite was prepared and tested for HA degradation. The photocatalytic reactions were performed using UV radiation. According to the results of the characterization analysis, KCC-1/CuS has been found to have excellent functional properties, in addition to the high applicability as a photocatalyst in treatment systems. The study on HA's degradation mechanism showed that the process of UV irradiation led to an excitation of the CuS (excitation electron from the valence band to conduction band) which led to the generation of high reactive radicals $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ through oxidation/reduction processes. Results showed that maximum degradation efficiency of HA equal to 89.5% was achieved at the optimum condition of 2 mg/L HA concentration, pH = 3, catalyst dose = 0.1 g/L, and UV irradiation time = 90 minutes.

From this study, the photocatalytic process, using KCC-1/CuS under irradiation by UV light, can be suggested as an efficient technology to remove HA from aqueous solutions.

Acknowledgments

The authors express their sincere thanks to the Birjand University of Medical Sciences for the technical and financial support.

Ethical Approval

The Ethics Committee of Birjand University of Medical Sciences approved the study with the ethical code of Ir.bums.REC.1398.18.

Consent to participate

Not applicable

Consent to publish

Not applicable

Authors Contributions

Mohammadi, N carried out the experiments and wrote the manuscript. Naghizadeh, A and Allahresani, A supervised the project.

Funding

Birjand University of Medical Sciences has provided financial support for this research.

Competing interests

There is no competing of interest

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

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Figures

Figure 1

FTIR spectrums of KCC-1 (a) and KCC-1/CuS (b) nanocomposite

Figure 2

Schematic representation of the reactor used for the photocatalytic degradation of HA.

Figure 3

TEM images of KCC-1/CuS nanocomposite

Figure 4

TGA analysis of KCC-1/CuS nanocomposite

Figure 5

EDS results of KCC-1/CuS nanocomposite

Figure 6

XRD patterns of 7 KCC-1/CuS NPs

Figure 7

a) The pHzpc of KCC-1/CuS nanocomposite b) Effect of pH in photocatalytic degradation of HA by KCC-1/CuS (HA concentration: 15 mg/L, catalyst dosage: 0.03 g/L).

Figure 8

Effect of catalyst dosage in photocatalytic degradation of HA by KCC-1/CuS (HA concentration: 2 mg/L, pH=3)

Figure 9

Effect of HA concentration in photocatalytic degradation of HA by KCC-1/CuS (catalyst dose: 0.1 g/L, pH=3)