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Article

Removal of sulfur ions from crude oil using copper Oxide Nanoparticles

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Abstract

The present study was designed to investigate the effectiveness of the adsorption desulfurization of crude oil using CuO-NPs. The prepared of nanoparticles using a sol-gel method was subjected to a novel analysis comprising standard analytical methods, including XRD, FESEM, and EDX, to identify the crystalline phase, morphological, and referring contained of the element in the particles. Hence, the XRD of crystalline planes of CuO exhibited peaks of the monoclinic structure at 31.6°, 45.4°, 56.4°, 66.3, and 75.2° corresponding to indexed planes of 110, 112, 202, 220, and 004, respectively. The average size of CuO-NPs was found to be 34 nm based on the Debye-Scherrer equation. Comparatively, the FESEM demonstrated through agglomerated spherical shape is shown at different magnifications. The particle size was found to follow an interval ranging from 42.43 to 87.09 nm. The elemental composition of EDX profiles was composed of

Cu standing at 80.6%, O at 13.9 %, and 5.5 C%. The peak of Cu along with O shows sound evidence, suggesting that it contains nanocrystals made up of CuO nanoparticles at 1:1. In summary, the lowest removal efficiency was found at the highest temperature of 328K, 150 minutes of time, and 50 mg of adsorbent, while the removal efficiency increased as the temperature fell, the adsorbent was increased, and the contact time increased. Thus, the scavenged material was providing effective removal with optimal results and possibilities to develop for industrial applicability.

Keywords: Adsorption, CuO-NPs, desulfurization, Crude oil.

INTRODUCTION

The need for crude oil as a principal energy source was perpetually rising, propelled by economic expansion. This has led researchers to create desulfurization technologies to enhance crude oil quality and diminish its Sulphur level [1, 2]. High levels of sulfur in crude oil cause negative effects in refining processes, most notably corrosion problems in pipes and equipment, in addition to its environmental damage [3, 4]. Heavy crude oil is characterized by basic properties, including: higher viscosity, higher density, greater acidity and more sulphur content. The process of hydrodesulfurization (HDS) is a typical industrial technique carried out in oil refineries to reduce Sulphur levels. Nevertheless, this method is expensive, needs a severe operating environment (in terms of temperature and pressure), and cannot remove aromatic cyclic Sulphur compounds such as thiophene, benzothiophene or dibenzothiophene [5]. Instead of hydrogen-desulfurization, other methods of sulfur removal have been developed, such as solvent extraction, adsorption, photo-oxidation and ionic liquids [6, 7]. Adsorption was regarded as a very promising technique owing to the potential use of many adsorbent materials, which must possess an active surface, extensive surface area, and appropriate pore size distribution [7]. The sulfur removal adsorption technology depends on the nature of the adsorbent and on its physical and chemical properties in removing organo-sulfur compounds [8]. Several types of adsorbents were utilized for this purpose, including activated carbon [14], Y-type zeolite [15], and nano-materials such as copper oxide nanoparticles. A number of researchers have investigated the removal of sulphur from diverse petroleum derivatives by adsorption technology. Nevertheless, prior research has not examined the extraction of organic sulphur compounds from heavy crude oil. This study elucidates the desulfurization of heavy crude oil from the East Baqubah field, which has a sulphur content of 4.31%, employing adsorption technology with nanocupric oxide. The study investigated the impact of adsorption duration and changed matrix concentration on the efficacy of the removal process.

MATERIALS AND METHODS

Synthesis of copper oxide nanoparticles (CuO-NPs)

Copper oxide nanoparticles have been synthesized utilizing the sol-gel method with [$Cu(NO_3)_2 \cdot 3H_2O$] and dissolved citric acid in ionic water at a concentration of 0.1 M. The solution was stirred magnetically at 90 °C for 2 hours. The agitation continued until gelation was place. Thereafter, the gel was allowed to ignite at 110°C. The material underwent additional annealing for 4 hours at 450°C to yield crystalline CuO nanoparticles [9].

Characterization of CuO-NPs

In this study, A variety of approaches were employed to characterize copper oxide nanoparticles. X-ray diffraction (XRD) utilizing a CuO x-ray tube at 1.54060 Å, with a voltage of 40.0 kV and a current of 30.0 mA, was employed to ascertain the mineral composition of the raw copper oxide nanoparticles. The chemical composition was analyzed using energy dispersive spectroscopy (EDS). The surface morphology of the copper oxide nanoparticles was examined utilizing a scanning electron microscopic (SEM) with a silicon drift detector (SDD-X-Max, Oxford Instruments Group [10].

Desulfurization process

The crude oil desulfurization process involved mixing 20 ml of heavy crude oil with CuO-NPs at different concentrations (0.6, 0.9, 1.2, and 1.5 g) inside an Erlenmeyer flask. The samples were then ultrasonicated for several periods of time (1, 2, 3, 4, and 5 hours) at a constant water temperature of 40 °C. The mixture was then allowed to settle to a slurry, while the treated crude oil was subsequently used for sulfur content analysis.

Determination of removal rate (R %)

The removal percentage (R %) was determined utilizing equations [11, 12].

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \ldots\ldots \textbf{(2.1)}$$

Wherease :

R%: Proportion of metal removed.

C_o: First concentration of metallic ion, expressed in mg/L.

C_e : Concentration of metallic ions post-adsorption, (mg/L).

RESULTS AND DISCUSSION

Characterization of the adsorbent

Different techniques and instruments were used to characterize the **TiO_2 NPs** adsorbent and as:

X-ray diffraction

The adsorbents were characterized using XRD, and the crystal size was measured with a powder X-ray diffractometer. Where Cu irradiance was utilized (k Cu = 1.5406 Å). Figure 1 illustrates the XRD pattern of CuO nanoparticles, Distinct peaks at 2θ signify the crystalline characteristics of CuO nanoparticles. The study of crystalline planes of reveals peaks at 31.6, 45.4, 56.4, 66.3 and 75.2 that indexed planes (110), (112), (202), (220) and (004), respectively, was employed to delineate the monoclinic structure of CuO-NPs [13, 14]. This corresponds to the six peaks documented in the XRD pattern, with no supplementary peaks seen, suggesting the phases of CuO NPs nanostructures [15] . The particle sizes were determined using the following Deby-Sherrer formula :

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \quad \textbf{......(3.1)}$$

Where:

D: represents the size of crystallite.

λ :represents the wavelength of radiation.

θ :represents Bragg's angle.

β: is the full width at half maximum (FWHM) **[16].**

The size of the particles for CuO nanoparticles is determined to be 34.6 nm. The material's nanocrystalline characteristics are evidenced by pronounced peaks in XRD samples and particle sizes less than 100 nm.

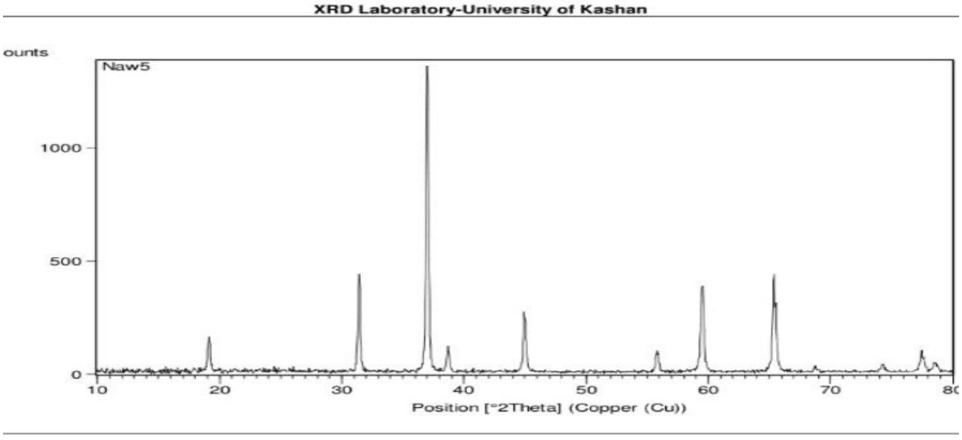

Figure 1. XRD of CuO-NPs synthesis

Field Emission Scanning Electron Microscopic (FESEM)

Illustrates the surface morphology of CuO-NPs through FESEM. The FESEM examination was conducted at various magnifications, revealing micrographs that depict agglomerated spherical particles. FESEM pictures indicated that the average size of CuO-NPs is ranged from (42.43-87.09) nm **[17]** as shown in Figure 2.

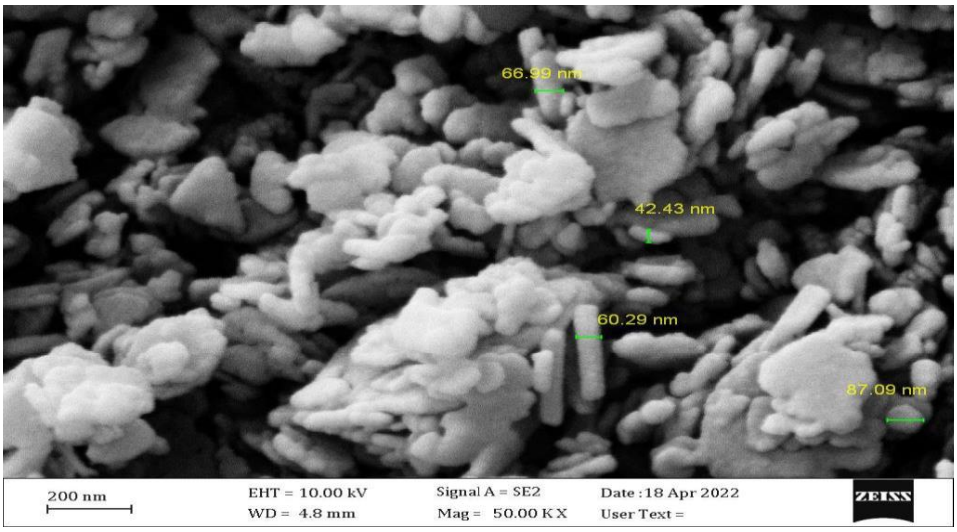

Figure 2. FESEM of CuO-NPs synthesis

Energy – dispersive X-ray Analysis Spectroscopy (EDXA)

EDX was employed to identify the components contained in the CuO-NPs sample. Figure (3) indicates that the EDX data comprised primarily Cu (80.6%), O (13.9%) and C (5.5 %). The peaks corresponding to Cu and O provide compelling evidence that the nanocrystals consist solely of CuO-NPs **[18]**.

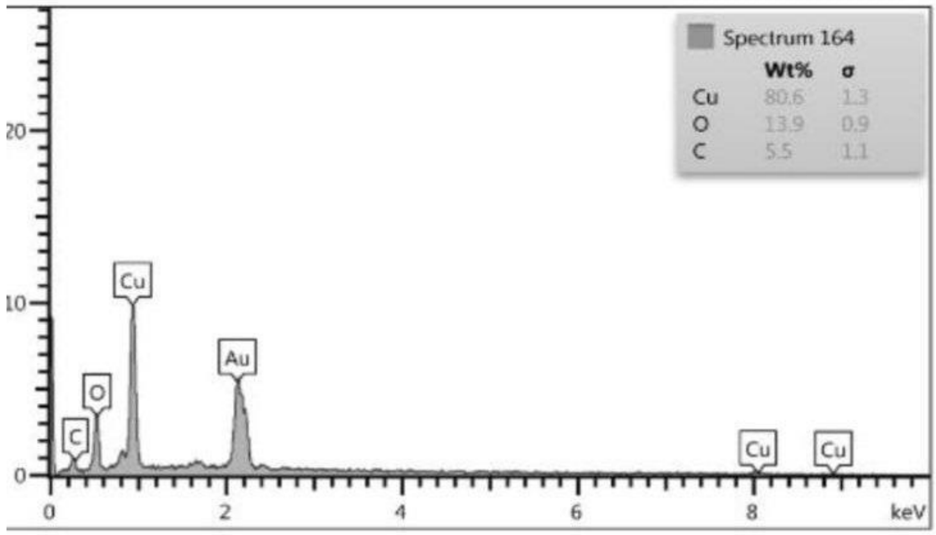

Figure 3. EDXA of CuO-NPs synthesis

Optimization of conditions

Effect of Temperture

Table 2 shows the effect of temperature (298- 338)K on desulfurization of heavy crude oil with using CuO nanoparticles. The results indicated that at a low temperature (298 K), the residual sulfur content was 1.664%, meaning the removal efficiency reached 6.51%, which is the highest value compared to other temperatures.

Table 2. Impact of temperature on the adsorption of sulphur compounds using CuO-NPs

T.K	S% Initial	S% Remain	R %
298	1.78	1.664	6.516
308		1.682	5.505
318		1.703	4.225
328		1.725	3.089
338		1.770	0.561

The results showed that the best adsorption was achieved at low temperature (298 K), and as the temperature gradually increased to (308–338 K), a gradual decrease in the adsorption efficiency was observed (from 5.50% at 308 K to only 0.56% at 338 K). These results indicate that the adsorption process is more effective at low temperatures, as its action diminishes with rising temperature. This is due to the fact that elevated temperatures result in a rise in the kinetic energy of sulphur molecules, which reduces their stability on the surface of the CuO nanoparticles and weakens the physical/chemical attractive forces responsible for the adsorption process. The results of the current study are consistent with a study conducted by Saod *et al*., 2023 [19] who indicated that temperature is inversely proportional to the adsorption efficiency. These results are consistent with those of Florent *et al*. (2020) when studying the adsorption of H_2S onto synthetic porous materials, where they observed that the adsorption capacity gradually decreased with increasing temperature from 25 °C to 100 °C, which they attributed to the exothermic nature of the process[20]. Similar studies using activated carbon or metal oxides have shown that adsorption decreases with temperature due to weakening van der Waals forces and a decreasing equilibrium constant.

Effect of time

Table 1, shows the effect of contact time on sulfur removal from heavy crude oil at 25°C. The results indicate that increasing the contact time between the copper nanoparticles and the sulfur compounds resulted in a gradual increase in the removal ratio (R%). The removal ratio increased from 8.82% at 10 minutes to 21.40% at 50 minutes, with the residual sulfur concentration decreasing from 1.623 to 1.3995. This indicates that the adsorption process continues to increase with time until higher levels of removal are reached. Sulfur removal occurs through adsorption, and adsorption increases with time up to 50 minutes.

Table 1. Impact of contact duration on the adsorption of Sulphur compounds using CuO-NPs

Time (min)	S (initial)	S (remain)	R%
10	1.78	1.623	8.820
20		1.570	11.797
30		1.525	14.325
40		1.448	18.651
50		1.3995	21.404

When copper nanoparticles initially come into contact with sulfur compounds in crude oil, A significant quantity of active sites on the adsorbent's surface remains unoccupied, facilitating the fast binding of sulphur compounds owing to the electrostatic attraction among the positively charged copper nanoparticles and the negatively charged sulphur particles [21]. Over time, the molecules continue to diffuse from the solution to the particle surface and occupy more of these active sites[22]. Therefore, the longer the contact time, the greater the amount of adsorbed molecules and the lower the residual concentration in the solution, reflected in a higher adsorption efficiency (R%). The results of the current study are consistent with Odin's study, which confirmed that the adsorption capacity increased significantly within 20 minutes, due to two mechanisms affecting adsorption[23]. During the first five minutes of the reaction, cation exchange occurred, while the subsequent adsorption mechanism was associated with the formation of surface complexes in the inner shell[24]. Majid and Fakhry investigated the temporal effects of nickel/iodine zeolite as an adsorbent and noted that the desulfurization process escalates with time, reaching its zenith after 4 hours [25].

Effect of dose adsorbent

Table 3 shows the effect of different concentrations of CuO nanoparticles (50-250) mg on sulfur removal at 298 K for 50 min. The findings indicate that augmenting the quantity of CuO nanoparticle adsorbent resulted in a progressive reduction of residual sulphur compound content in the solution and an enhancement in removal efficiency. At 50 mg, the removal rate was low (15.11%), then gradually increased with increasing amount, reaching 19.72% at 100 mg, 25.45% at 150 mg, 32.70% at 200 mg, and finally reaching the highest value at 250 mg, at 36.85%. This demonstrates that the adsorption efficiency improves with increasing adsorbent amount.

Table 3. Impact the adsorbent quantity onto the adsorption for Sulphur compounds using CuO-NPs

W (mg)	S (initial)	S (remain)	R%
50	1.78	1.511	15.112
100		1.429	19.719
150		1.327	25.449
200		1.198	32.696
250		1.124	36.853

The findings of the present investigation indicated that sulphur extraction from heavy crude oil enhanced with higher concentrations of copper oxide nanoparticles (CuO-NPs), attributable to the augmented surface area and active sites of sulphur compounds. Numerous studies have utilized copper oxide nanoparticles for sulphur removal from model petroleum; however, they have not implemented this approach in heavy crude oil. Our results are contrasted with prior studies to illustrate the impact of concentration on the desulfurization process [26, 27]. Alangari *et al*., Additionally, the impact of adsorbent dosage on sulphur removal was examined utilizing a model fuel with various concentrations of CuO-NPs, revealing that the efficiency of remove enhanced with increased adsorption dosage [28] . Meanwhile, Allah *et al.* did a study on the desulfurization of model oil utilizing activated carbon and CuO-NPs , confirming that an increase in the quantity of adsorbent results in a better removal rate [29].

CONCLUSION

Copper oxide nanoparticles (CuO-NPs), with stable structural properties and small nano-sized sizes, were shown to be highly efficient in removing sulfur from crude oil. The results indicate that these particles represent a promising alternative for removing pollutants from the environment.

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