RESEARCH PAPER

Removal of Cyanide from Water and Wastewater Using Nanocrystalline ZnO/NiO Mixed Metal Oxide Powder

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ABSTRACT

Increased demand for commodities as a result of the growing population has sped up industrialization. As a result of the expansion in industrial setups, there has been an increase in the generation of industrial waste. By polluting the water, air, and soil, these industrial pollutants seriously harm the ecosystem. Cyanide is one of the most significant environmental contaminants found in the sewage of various industries, and it can pollute water supplies in ways that are hazardous to both humans and the environment. There are numerous strategies to remove cyanide from aqueous media, however the majority of them are expensive. Consequently, this study's objective is to remove cyanide utilizing nanocrystalline ZnO/NiO mixed metal oxide powder (ZnO@NiO). The influence of the adsorbent, initial cyanide concentration, contact time, and pH were evaluated in discontinuous phase for the removal of cyanide from aqueous media utilizing ZnO@NiO nanocrystals under varied conditions. Adsorption equilibrium were investigated in this study. The results of the study showed that the removal efficiency increases with the increase in retention time and the amount of adsorbent. The maximum amount of cyanide removal was obtained at pH = 10, retention time of 90 minutes, cyanide concentration of 2.5 mg/liter, and the adsorbent weight of 1 g, which was more than 98%.

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INTRODUCTION

Every year, a large amount of waste from domestic sources and industrial agriculture enters the environment. These effluents contain a high concentration of organic and inorganic chemicals such as hydrocarbon solvents, heavy metals, insecticides, and dyes [1–3]. It is obvious that the presence of such pollutants results in health and

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environmental risks. Water pollution is one of the biggest problems caused by these pollutants [4]. Cyanide is a chemical substance that humans have made both naturally and artificially, and most of its compounds are highly toxic [5,6]. Among the compounds of cyanide, we can refer to hydrogen cyanide, which is in the form of gas, and cyanide salts such as sodium cyanide and potassium cyanide [7]. Among the main sources of cyanide in water, we can refer to the effluents of chemical and electroplating industries, car fuel, municipal sewage and insecticides [8]. This substance enters the body through drinking, inhalation and eating [9]. A large amount of this substance may affect the heart and brain and cause coma and then death in a short period of time. Cyanide has the potential to generate poison in the blood at a dosage of 0.05 mg/dl and will typically result in death at a concentration of 0.3 mg/dl [10,11]. The United States Environmental Protection Agency (USEPA) has determined the maximum allowable amount of cyanide in water to be 0.2 mg/liter [12]. Cyanide concentration in water and wastewater can be reduced by dilution, biological and chemical oxidation, precipitation and recycling methods [13,14].

Nanotechnology is a process that plays a key role in preventing pollution, identifying, measuring and purifying pollutants [15]. One of the technologies that has gained a lot of acceptance recently is the use of nanoscale particles for purification and removal of pollutants [16]. Due to their small size, large cross-sectional area, crystal form, unique network order, and as a result, high reactivity, nanoparticles can be used to purify and transform pollutants into harmless and less harmful substances [17]. Iron particles from industrial processes can be used as iron in the purification of pollutants. The mechanism of removal of pollutants by iron is reduction reactions or absorption process [18]. Particle size is a relatively important characteristic of particles in absorbing and reacting with pollutants. Among the methods that have been used to remove cyanide in the past, we can mention chlorination with high pH [19], use of SO_2/Air process [20] and use of electrochemical method [21], but each of these methods has its own disadvantages. Despite the fact that alkaline chlorination is frequently employed to remove cyanide, it will produce toxic cyanogens chloride and chloride disinfection byproducts [22]. Some researchers have also looked into more sophisticated oxidation procedures, such as photochemical oxidation and the use of ultrasonic waves to detoxify cyanide effluents [23–26]. But these are costly, cumbersome to use, and ineffective for treating cyanides. Adsorption is an appealing approach because of its high efficiency and low difficulty compared to the other ways that are available [27].

Adsorption is one of the ways that can be used for the removal of cyanide ions, and it has a high rate of removal efficiency. Adsorption is a viable option for the efficient elimination of cyanide ions. For the purpose of removing cyanide from effluents, several research groups utilized a variety

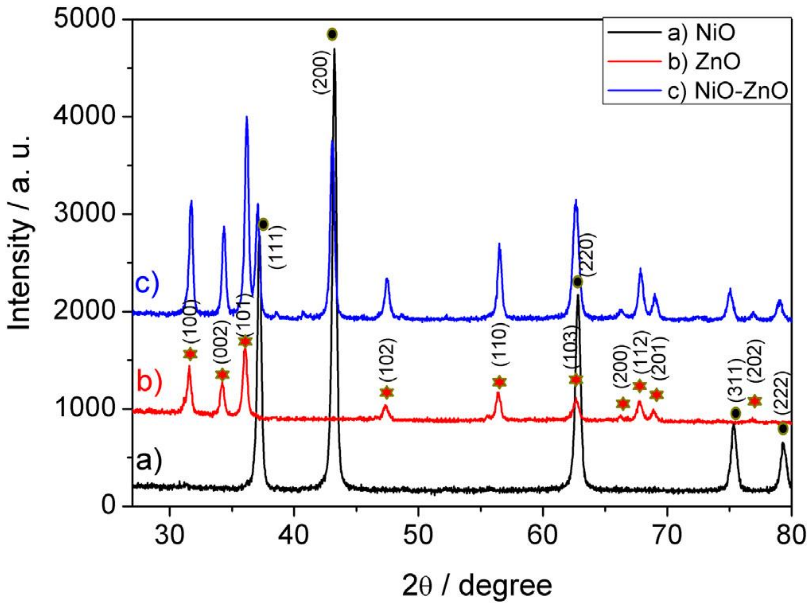

Fig. 1. XRD pattern: (a) ZnO, (b) NiO and (c) ZnO@NiO nanocrystals.

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of adsorbents, including different agricultural products [28–30]. Due to their affordability, green synthesis, non-toxicity, and non-hygroscopic nature, nano transition metal oxide materials like nickel oxide (NiO), copper oxide (CuO), and zinc oxide (ZnO) have recently gained a great deal of interest. Consequently, various metal oxides were used as sorbents or catalysts to remove cyanide [31,32]. For the electrochemical sensing of uric acid and dopamine, as well as for carbon monoxide (CO) optical detecting and xylene sensors, a hybrid NiO/ZnO nanoparticle was utilized [33]. A heterostructure of ZnO@NiO was also used for gas sensing [34]. The small size, the large cross-sectional area and as a result the high reactivity of these materials, the capacity to remain in suspension and easy transport by underground water, have increased their potential for use in water treatment. As a result, these materials are recognized as a flexible and expanding technology for in-situ remediation of contaminated groundwater. The purpose of this research is to investigate the effectiveness of nanocrystalline ZnO/NiO mixed metal oxide powder (ZnO@NiO) in removing cyanide in laboratory conditions.

MATERIALS AND METHODS

In order to produce nanocrystalline ZnO/NiO mixed metal oxide powder (ZnO@NiO), nickel chloride and zinc acetate were dissolved in deionized water at a molar ratio of 1:1 [35]. These two compounds were then combined with 0.1 mol/liter oxalic acid solution, mixed, and then subjected to treatment in a microwave oven. Fig. 1 displays the XRD (X-ray diffraction) patterns of ZnO@NiO, NiO, and ZnO.

The scanning electron microscope (SEM) was used to investigate the surface shape as well as the size of the as-prepared ZnO@NiO, NiO, and ZnO (Fig. 2). An LEO instrument model 1455VP was used to produce the SEM images.

Fig. 3 display the FTIR (Fourier-transform

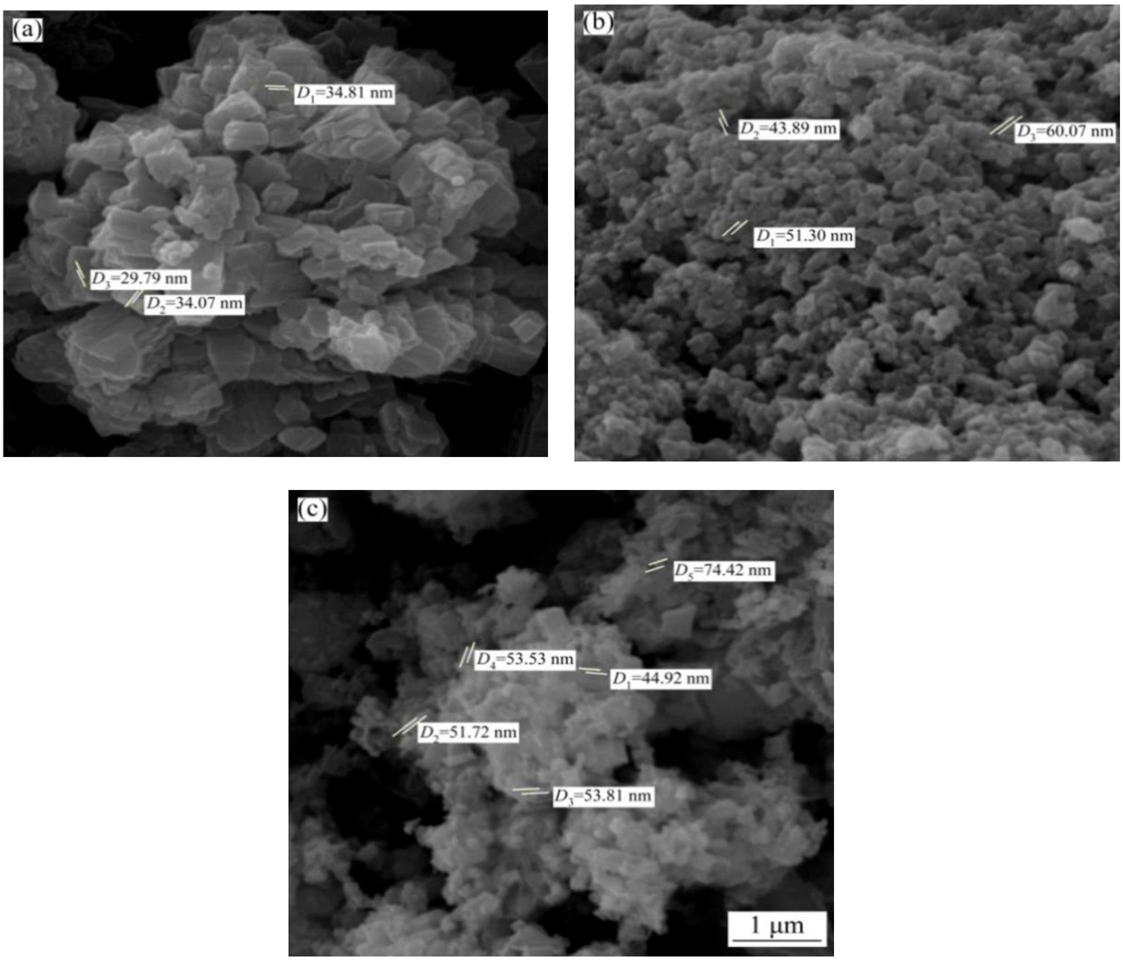
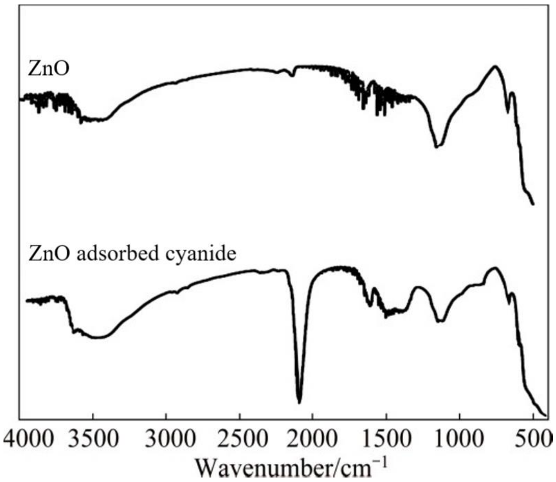
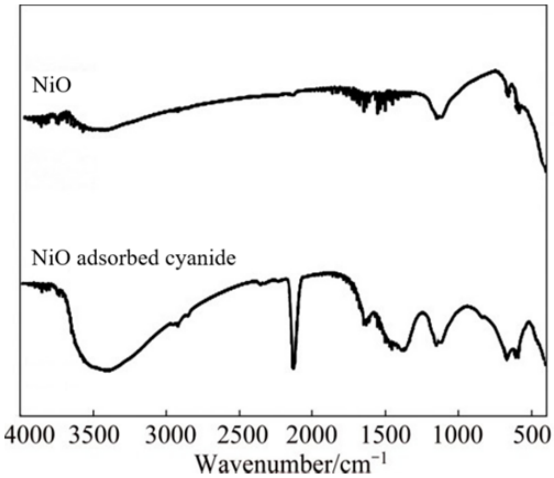


Fig. 2. SEM images: (a) ZnO, (b) NiO and (c) ZnO@NiO nanocrystals.



(a)



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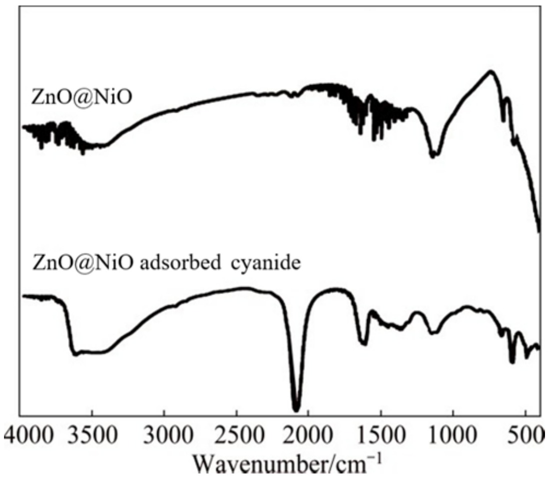

Fig. 3. FTIR analysis of: (a) ZnO, (b) NiO, and (c) ZnO@NiO.

infrared spectroscopy) absorption spectra of ZnO@NiO, NiO, and ZnO. O—H stretching and H—O—H bending vibrations in H2O are responsible for the large absorption peaks at 3400 and 3500 cm^{-1} and 1620 and 1640 cm^{-1}, respectively.

The stretching vibration mode of M—O (M=Zn, Ni) is attributed to the large absorption bands in the 400–850 cm^{-1} area; the M—O powders are nanocrystals as the breadth of the absorption band suggests. Cyanide solution was prepared in four concentrations of 2.5, 25, 50 and 75 mg/liter. Then the desired solutions were placed in contact with the desired concentrations in the range of 0.2 to 1 g/liter of the adsorbent at different contact times. Values of 2, 4, 6, 8 and 10 were determined for pH investigation, and 15, 30, 45, 60, 90, and 120 minutes were measured for retention time. A stirrer was used at a speed of 100 rpm for mixing. After the absorption process, the samples were centrifuged and measured by titration. In order to increase the accuracy, all the experiments were performed at the temperature of the laboratory environment and about 25^{o}C. A standard titrimetric method was used to measure cyanide [36]. After using the appropriate methods to purify the samples, 50 ml of NaOH solution was diluted, and 0.5 cc of an indicator solution was added to each of the targeted samples. The titration was performed using titrant and a silver nitrate standard until the color changed from canary yellow to pinkish brown [37]. These procedures were also used to prepare the control

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sample.

RESULTS AND DISCUSSION

By increasing the retention time in constant conditions, the removal efficiency increased (Fig. 4). The increase in the quantity of collisions between the pollutant and the adsorbent may be the reason of this increase in absorption. The best retention time was 90 minutes, which resulted in the maximum removal of 98%.

The results obtained according to Fig. 5 show that with the increase in the concentration of nanocrystals in constant conditions, the efficiency of cyanide removal has increased. Also, the most appropriate amount of absorbent weight of 1 g was chosen because the percentage of removal increased up to this amount. However, after that, the amount of turbidity in the liquid increased and the removal percentage did not increase significantly.

In order to investigate the effect of pH parameter on cyanide removal efficiency, studies were conducted in 4 pH ranges. The results related to the effect of pH changes on removal efficiency are shown in Fig. 6. The results showed that in constant conditions, pH = 10 is the most efficient in removal. At the initial cyanide concentration of 2.5 mg/liter, the weight of the adsorbent was 0.5 g, and the absorption rate of the pollutant was more than 98% in 90 minutes.

The obtained results show that the cyanide removal efficiency has increased by increasing the concentration of ZnO@NiO nanocrystals in constant conditions. The reason for this increase in efficiency is related to the increase in the amount of adsorbent and as a result, more collisions between the adsorbent and the pollutant, which results in more pollutant sticking to the adsorbent. However, it should be emphasized that while this increase in absorbance may, in certain cases, be advantageous, it may also be expensive or cause the residual solution to become more turbid. Regarding the contact time variable, the results of this study show that although the cyanide removal efficiency increases with the increase of contact time, the maximum amount of absorption occurs during the first 90 minutes. These results also show that in the absorption stages, diffusion in the thin layer, which is the first stage of absorption, happens faster, but penetration in the pores, which leads to more absorption in the internal surfaces of the absorber, happens with a delay. The delay about this absorber and pollutant was about 90 minutes. Contact time is one of the most important parameters in chemical reactions. Basically, in chemical reactions, an optimal contact time or equilibrium time can be defined for the desired reaction. The period of time known as equilibrium occurs when the rate of pollution elimination stabilizes. Also, in this research, a direct relationship was observed between the absorbent contact time variable and the removal efficiency.

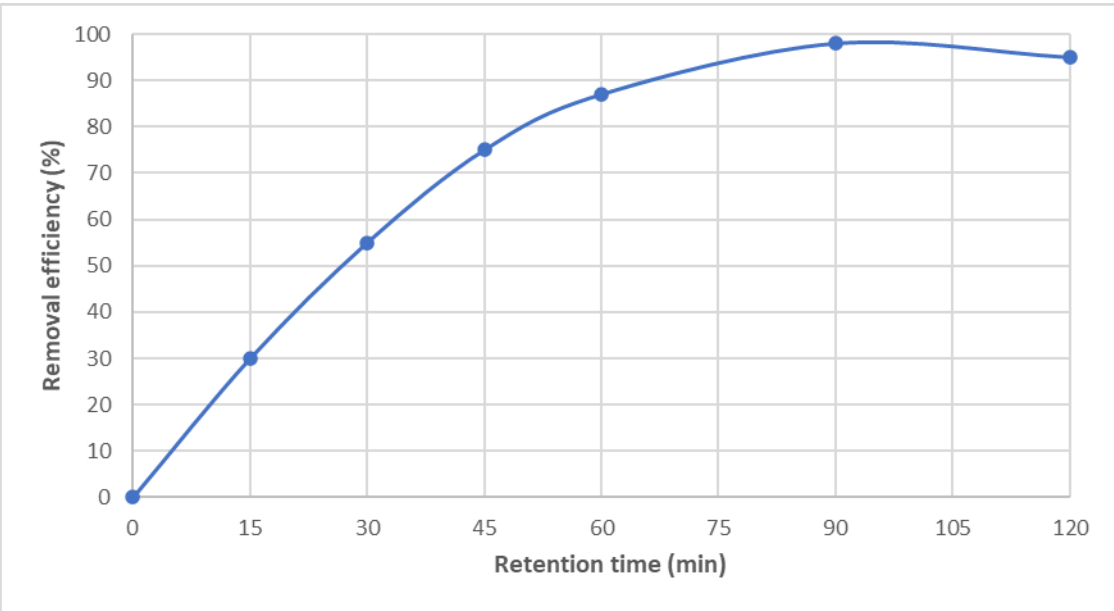

Fig. 4. Effect of contact time on cyanide removal efficiency (initial concentration of cyanide = 2.5 mg/liter, absorbent weight = 0.5 g, pH = 10)

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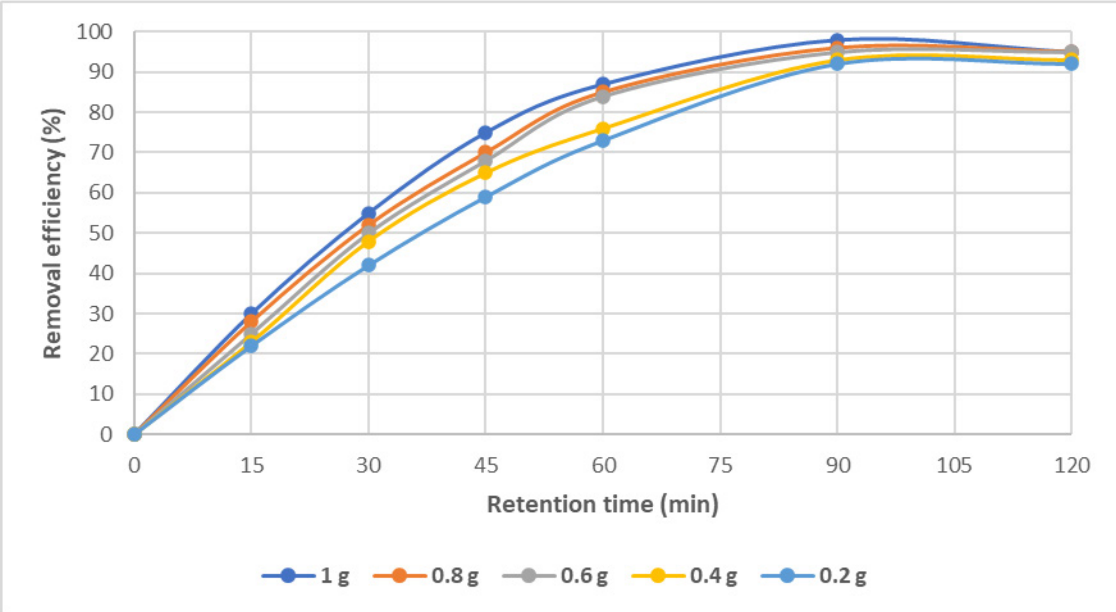

Fig. 5. Effect of adsorbent concentration on cyanide removal efficiency using ZnO@NiO nanocrystals (initial concentration of cyanide = 2.5 mg/liter, pH = 10).

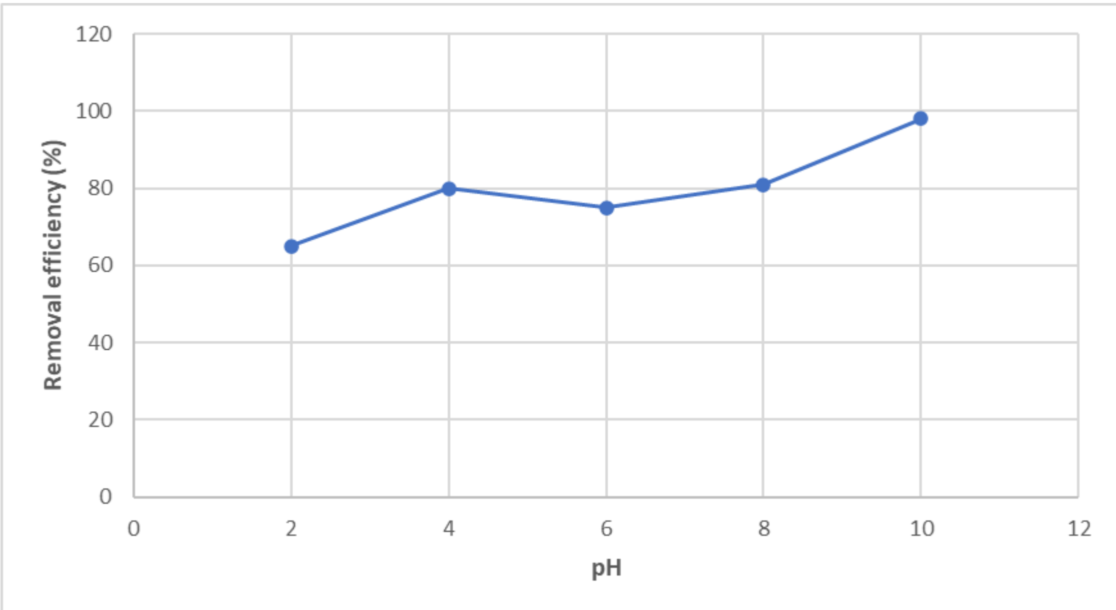

Fig. 6. Effect of pH changes on cyanide removal efficiency using ZnO@NiO nanocrystals (initial concentration of cyanide = 2.5 mg/liter, absorbent weight = 0.5 g, retention time = 90 min).

The reason for this can also be the increase in the contact time between the absorbent material and the pollutant. In the research conducted by Aigbe and Kavaz (2021) on the removal of lead with sawdust, a direct relationship between the contact time factor and the removal percentage

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was also observed [38]. Demcak et al. (2019) in another study on the removal of heavy metals from water environments with sawdust also found that the application of contact time will increase the efficiency [39]. According to the results, there is higher removal in alkaline pH than in acidic or neutral pH, which can be attributed to two factors: the higher the pH, the more cyanide forms CNO^- and precipitates, but if the pH is acidic, cyanide forms more HCN, which is less likely to precipitate in this form. In other studies, cyanide was removed using an ultrasonic approach [40]. The results revealed that cyanide has a high removal efficiency at a pH of 10.5, as in this situation, it transforms into the cyanide ion, which is also easily removed from aqueous environments.

CONCLUSION

The results of the study showed that the method of ZnO@NiO nanocrystals is a more suitable method for removing cyanide from industrial wastewater due to the reasons of higher removal of cyanide and the absence of related problems. It is a more suited procedure than the typical ones, which are unable to significantly diminish the high toxicity of cyanide. Additionally, the conventional approaches leave behind residues, which their removal presents more difficulties. Therefore, ZnO@NiO nanocrystals are a viable choice for cyanide reduction in water environments where cyanide contamination is a problem.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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