ABSTRACT: Cadmium ion is toxic to organisms and shows persistence because of its nondegradability. Photoreduction of the cadmium ion (Cd(II)) was studied using a bentonite-supported Zn oxide (ZnO/BT) photocatalyst in an aqueous medium under ultraviolet light. The prepared ZnO/BT photocatalyst was characterized by diffuse reflectance spectroscopy, field-emission scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, photoluminescence spectroscopy, transmission electron microscopy, energy-dispersive spectroscopy, and Brunauer−Emmett−Teller/Barrett−Joyner−Halenda analysis. The effects of main parameters including pH, contact time, initial concentration of cadmium(II) ion, light intensity, temperature, and the photocatalyst dosage were investigated for obtaining appreciate reduction/removal efficiency. The maximum reduction/removal efficiency of 74.8% was obtained at optimized values which were found to be at pH 5, 6 h contact time, 6 ppm Cd(II) ion, 200 W UV light, 45 °C temperature, and 4 g/L of ZnO/BT. Reduction/removal of Cd(II) was significantly affected by light intensity so that the increment in UV intensity from 0 to 200 increased the reduction/removal efficiency from 61.2 to 76.8%. This study reports an inexpensive and environmentally friendly photocatalyst for Cd²⁺ reduction in real samples and prospective photoelectric materials.

1. INTRODUCTION

Heavy metals are referred to as a group of metals having more than 6000 kg/m³ density with a specific gravity higher than 4 g/cm³.¹ Heavy metals including lead, mercury, copper, cadmium, vanadium, nickel, chromium, and so forth exist in the wastewater of many industries such as the zinc extraction industry, oil refining, pulp and paper, pharmaceutical, dyeing industry, and plastic products.²⁻⁶ From the environmental, health, and hygiene points of view, heavy metals and many of their compounds are considered as toxins for organisms because of their harmful effects.⁷⁻⁹ As mentioned above, these metals easily enter the body by agglomerating in various tissues such as adipose tissues, muscles, bones, and joints via sedimentation and cause numerous diseases and many side effects. The presence of heavy metals in the aquatic environment contributes to the appearance of environmental issues and side effects for those living in that ecosystem.¹⁰ Neurological disorders are the main effects of these metals on human.¹¹ Heavy metals substitute the minerals in the body, leading to disorder in the equilibrium of organisms and create harmful issues.¹² Among the heavy metals, cadmium is a highly toxic metal, which could be introduced into the aquatic system via agricultural practices and chemical industries including electroplating, metallurgical alloying, metal-finishing, ceramics, photography, cadmium-containing pigments, textile printing, plastic production, cadmium-containing phosphate fertilizers, refined petroleum products, and detergents.¹¹,¹² Therefore, it is necessary to apply acceptable methods for the removal of cadmium species from the aquatic environment as well as ecosystems.¹³ Conventional treatment methods include precipitation, ion exchange, reverse osmosis, and adsorption, and biological processes that have an inadequate affinity and selectivity for the reduction of residual cadmium concentration were imposed by environmental and health regulatory bodies.¹⁴⁻¹⁶ In addition, in these methods, Cd(II) in its toxic form is only captured and transformed from one phase to another.¹⁷ Therefore, it is important to develop a new method for reducing Cd(II) to Cd(0), which is nontoxic.¹⁸ The photocatalytic reduction method is a clean, fast, green, and low-cost purification technique for the metal ion treatment process.¹⁹⁻²¹ In the photocatalytic reduction/removal technique, pollutants were directly reduced to the metallic phase, which makes this property "green chemistry".²² In photo-reduction/removal, heterogeneous photocatalysts can undergo both oxidation and reduction reactions under light energy.
Light energy is applied for producing the electron–hole pairs in photocatalysis, such as a semiconductor material.\(^2\) In this case, the photogenerated electrons in the conduction band (CB) of semiconductors are consumed by metal ions and reduced to the nontoxic form.\(^2\) In a decade, photoreduction/removal has been extensively studied for the removal of several heavy metals, such as chromium, nickel, cadmium, and mercury.\(^2\) There are several reports on few semiconductor photocatalysts under UV light for cadmium ion reduction/removal.\(^2\) The Cd(II) photoreduction process requires hole scavengers such as formic acid, three ethanolamines, and methanol to initiate the photoreduction process.\(^2\) Hole scavengers mainly suppress the charge carrier recombination to accomplish the photoreduction.\(^2\) They also produce secondary reducing hydroxyl and carboxyl radicals, which contribute to the photoreduction/removal process.\(^3\) In this process, selection of an efficient photocatalyst is important. Bentonite (BT) as one of the clays possesses certain properties such as low cost, high mechanical and chemical stability, availability, affordability, ion-exchange capability, and environmentally friendly nature, which make it an ultimate choice as the catalyst support.\(^4\) The photoreduction/removal efficiency strongly depends on the catalyst physical features such as band gaps.\(^2\) Therefore, for improving the recombination rate of photogenerated electrons and holes on BT and its activity in the UV region, its modification is very necessary.\(^2\) ZnO as a low band gap material and UV-driven agent has attracted interest because of its low toxicity.\(^5\) Therefore, in this research, it has been attempted to photoreduce cadmium ions using ZnO supported on BT (ZnO/BT) in a photocatalytic system to improve the adsorption and increase the reduction efficiency because of its high sensitivity to light and high contact surface. To the best of our knowledge, while several performances of the photocatalytic systems have been reported, this research aimed at investigating the photoreduction/removal process along with the physisorption of pollutants of BT, pure ZnO, and BT/ZnO (Figure 1) indicated a broad absorption peak of around 3430 cm\(^{-1}\) attributed to the stretching vibration of O–H groups, and the bands at about 1645 cm\(^{-1}\) are attributed to the H–O–H bending vibrations of adsorbed H\(_2\)O for all samples. In the spectrum of BT, the peak at 3610 cm\(^{-1}\) corresponds to the Al–O–H stretching vibration, while the stretching vibrations of Si–O–Si bonds have emerged at 1030 cm\(^{-1}\), which are characteristic of phyllosilicate minerals, as well as the bands at 465 and 521 cm\(^{-1}\) correspond to Si–O–Si and Al–O–Si bending vibrations. The band at 630 cm\(^{-1}\) is assigned to the out-of-plane vibrations of coupled Al–O and Si–O, and the band at 780 cm\(^{-1}\) is attributed to quartz admixture BT. The band at 840 cm\(^{-1}\) is assigned to the bending vibration of Al–MgOH, while the spectral band at 905 cm\(^{-1}\) reflects the stretching vibration of Al–O–(OH)–Al. For pure ZnO, the band at about 550 cm\(^{-1}\) is assigned to the Zn–O bending vibration, while the band at 864 cm\(^{-1}\) is due to the symmetric stretching vibration of O–Zn–O. One strong band at 1087 cm\(^{-1}\) is attributed to the asymmetric stretching of P–O–P groups. All the characteristic peaks of pure BT and ZnO were seen in the BT/ZnO hybrid composite photocatalysts, which confirm that ZnO microcubes (MCs) have been successfully attached to the exfoliated BT. Morphological characteristics of BT and the BT/ZnO nanocomposite were studied by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) (Figure 3). BT has a porous structure, suitable for ZnO immobilization. ZnO was successfully supported on the BT surface. The FESEM images showed

![Figure 1. XRD pattern of BT, ZnO, and BT/ZnO samples.](https://dx.doi.org/10.1021/acsomega.0c01219)

![Figure 2. FTIR spectra of the as-prepared samples.](https://dx.doi.org/10.1021/acsomega.0c01219)
that BT has a heterogeneous zigzag surface as well as grooves and cavities and the BT matrix is covered by ZnO particles that occupy the pores (Figure 3a,b). Figure 5c shows the growth of smooth ZnO MCs on the heterogeneous zigzag surface of BT, as well as the cubic structure of ZnO was proved by TEM images (Figure 3d).

The optical absorption property of BT and ZnO/BT is a key factor that determined their photocatalytic performance. UV–vis diffuse reflectance spectroscopy (DRS) (Figure 4a) indicated strong absorption with an absorption edge at about 400 nm, which is in agreement with the results reported previously for each BT and ZnO. While, after ZnO was supported on BT, the absorption edge of BT/ZnO was not shifted, the absorbance was enhanced in comparison with that of pure BT. This implied that BT/ZnO might use a UV spectrum more efficiently, leading to a higher photocatalytic activity. For final confirmation, a Tauc plot (Figure 4b) was drawn, and band gaps of BT and BT/ZnO were found to be 3.2 and 3.18 eV, respectively, which can be active in the UV region.

The recombination of photogenerated electron–hole pairs is an important parameter that proves the photocatalytic performance of photocatalysts. Generally, photoluminescence (PL) spectroscopy was performed to investigate the separation efficiency of photogenerated electron–hole pairs. In this case, a high fluorescence intensity generally corresponds to the significant recombination of electron–hole pairs. Therefore, as shown in Figure 4c, the main emission peak for BT is centered at approximately 425 nm. The broad and low-intensity peak for pure ZnO arising from the oxygen vacancies of its lattice extremely quenches the BT emission at a similar emission position. This result indicates that the BT/ZnO composite possesses a lower electron–hole recombination rate than BT.

To investigate any changes to the surface property of BT after the ZnO support, the Brunauer–Emmett–Teller (BET) surface areas of BT and the BT/ZnO composite were...
determined (Figure 5). The BET surface areas of pure BT and BT/ZnO were found to be 110.1 and 69.5 m$^2$ g$^{-1}$, respectively, which suggest that supporting of ZnO into exfoliated BT layers decreases the surface area of the BT/ZnO composite significantly, while reactive sites for Cd$^{2+}$ capture were increased. A decrease in the surface areas was observed in the clay composites. This is due to the deposition of the ZnO microparticles on the clay surface, which filled the mouth pore sites of the clay and also contributed to the increase in pore size. Therefore, with more microparticles loaded on the clay surface, it is implied that most spaces of the interparticle pores are occupied by the loaded microparticles in which the pore volumes for BT and ZnO/BT were found to be 0.022 and 0.018 cm$^3$ g$^{-1}$, respectively. The distribution of microparticles into the interparticle pores results in an enlargement of the corresponding pore size, in which the pore diameters for BT and ZnO/BT were found to be 8.5 and 14.3 nm, respectively. The high surface area retained in the BT/ZnO composite is beneficial for the enhancement of capturing and photoreduction activity.

2.2. Effect of the Operational Parameter on Cd(II) Photoreduction/Removal Process. The surface charge of photocatalysts and their ionization degree are changed by variation in pH. Therefore, the photoreduction of the Cd(II) ion is highly affected by this parameter. The effect of pH on Cd(II) photoreduction on the BT/ZnO composite and the parent semiconductors (Figure 6a) was investigated at various pH values of 3, 5, 7, and 9, while other parameters such as initial cadmium concentration, temperature, the stirring rate, and the photocatalyst dosage were constant at 5 ppm, 65 $^\circ$C, 80 rpm, and 2 g/L, respectively. As can be seen, the highest photoreduction degree was seen at the pH value of 5 as almost 70.6% for BT/ZnO, while for pure ZnO and pure BT, a lower rate was obtained. The degree of photoreduction was enhanced by about 4% by increasing the pH from 3 to 5, which was increased by increasing the pH from 5 to 7. Moreover, by enhancing the pH value from 7 to 9, the degree of photoreduction was increased. It has been suggested that the tendency of the metallic cation toward photoreduction is significantly dependent on their tendency toward hydrolysis reactions with a solution. Metallic cations in aqueous solutions are generally hydrolyzed according to the following reaction:

$$M^{2+} (aq) + nH_2O = M(OH)^{2-n} + nH^+$$

The dispersion of hydroxyl complexes is dependent on both the pH of the solution and stability. The requirement pH for Cd(OH)$_2$ precipitation was found to be 7.6, which can be observed at pH higher than this value; because of the precipitation of Cd(OH)$_2$, the photoreduction efficiency was decreased. In addition, in low pHs, protonation of ZnO/BT causes repulsion force between Cd(II) and protonated ZnO/BT and decreases the photoreduction—removal efficiency. After evaluating the effect of pH on cadmium photoreduction and detection of the optimum value, the effect of temperature on the photoreduction of the BT/ZnO composite and the parent semiconductors was investigated at various temperatures of 15, 30, 45, and 60 $^\circ$C, while other parameters were constant at the above-mentioned conditions (Figure 6b). As can be seen, by increasing the temperature from 15 to 30 $^\circ$C and also from 30 to 45 $^\circ$C, the degree of photoreduction on BT/ZnO was enhanced, while for pure ZnO and pure BT, a lower rate was obtained. In addition, it was decreased in the case of temperature rise from 45 to 60 $^\circ$C. The optimum
degree of photoreduction was found to be 45 °C for BT/ZnO. The increment in photoreduction by temperature rise might be due to the variations in the pore size of the ZnO/BT photocatalyst, which may cause diffusion into the particles or pores or increment in the cathode chemical ratio of metal to the surface, resulting in a type of chemical equilibrium which enhances the adsorption capacity during photoreduction.\textsuperscript{44} In this type of photocatalysis, the presence of dissolved oxygen will enhance the formation of an essential reaction rate so that the higher temperatures will reduce the amount of dissolved oxygen and that the reaction rate will decrease. Because diffusion is an endothermic phenomenon, the diffusion rate of ions in the external mass-transfer phenomena is increased by temperature.\textsuperscript{45}

The effect of initial cadmium concentration on the photoreduction of Cd\textsuperscript{2+} on the BT/ZnO composite and the parent semiconductors was investigated at various initial cadmium concentrations of 3, 6, 9, and 12 ppm, while other parameters were constant at the above-mentioned levels (Figure 6c). As can be seen, by increasing the initial cadmium concentration, the cadmium photoreduction was increased, while it was decreased in higher levels. The highest cadmium photoreduction efficiency was equal to 82.5% at 6 ppm for BT/ZnO, while for pure ZnO and pure BT, a lower value was obtained. At low initial concentrations, adequate sites are available for the physisorption of Cd(II) ions; hence, the degree of photoreduction is higher than other levels. At high concentrations of cadmium ions, the number of ions is more than free sites, and as a result, the degree of photoreduction is lower than other levels.\textsuperscript{46}

To monitor the effect of the ZnO/BT photocatalyst dosage on Cd(II) photoreduction on the BT/ZnO composite and the parent semiconductors, various parameters such as initial cadmium concentration, temperature, contact time, stirring rate, and pH were kept constant at the above-mentioned levels (Figure 6d). As can be seen, the degree of Cd(II) photoreduction has enhanced by increasing the ZnO/BT photocatalyst dosage from 1 to 8 g/L, and the highest degree of photoreduction was equal to 71.5%, which was obtained at 4 g/L ZnO/BT photocatalyst dosage, while for pure ZnO and pure BT, a lower value was obtained. The degree of Cd(II) photoreduction is enhanced by increasing the ZnO/BT photocatalyst dosage because of higher availability of changeable sites or higher surface area to speed ratios.

The effect of various contact times as 4, 6, 8, and 10 h on Cd(II) photoreduction on the BT/ZnO composite and the parent semiconductors was studied, while other parameters were kept at the optimum level (Figure 6e). As can be seen, increasing the contact time from 4 to 10 h has enhanced Cd(II) photoreduction on the BT/ZnO composite from 64.3 to 71.85%, while for pure ZnO and pure BT, a lower value was obtained. No remarkable variation (almost 0.6%) was observed in Cd(II) photoreduction in the range of 6–10 h. The highest degree of Cd(II) photoreduction was 61.8% at 10 h. The required contact time to reach equilibrium is dependent on the initial cadmium concentration, while the degree of Cd(II) photoreduction is increased by contact time until reaching equilibrium.\textsuperscript{47} The optimum time to achieve equilibrium in this study was 6 h.

In this section, the effect of applied light intensity Cd(II) photoreduction on the BT/ZnO composite and the parent semiconductors was investigated. Light intensity was changed as 50, 100, and 200 W, while other parameters were kept at optimum levels (Figure 6f). It can be seen that Cd(II) photoreduction has increased by enhancing the light intensity, and the highest degree of Cd(II) photoreduction was found to be 76.8% at a light intensity of 200 W on the BT/ZnO composite, while for pure ZnO and pure BT, a lower value was obtained. As the light intensity was increased from 0 to 100, Cd(II) photoreduction was not significantly changed. However, by enhancing the light intensity from 100 to 200, the degree of Cd(II) photoreduction was increased from 62.5 to 76.8%. In general, as the light energy becomes higher than that of the semiconductive bond, both electron pairs of the pore (e/h\textsuperscript{+}) are formed in the direction of zinc oxide’s conductivity and migrate to the semiconductive surface, reducing or oxidizing the species in the solution with high efficiency.\textsuperscript{48} Hence, Cd(II) photoreduction was increased by increasing the photocatalytic light irradiation. Consequently, according to the various experiments performed in this research, the optimum values for initial cadmium concentration, pH value, process time, light intensity, photocatalyst dosage, and temperature were determined to be equal to 6 ppm, 5, 6 h, 200 W, 4 g/L, and 45 °C, respectively.

2.3. Photoreduction Mechanism of Cd(II) under UV Light. The high BET surface of BT/ZnO photocatalysts provided more surface active sites for physisorption and photoreduction of Cd\textsuperscript{2+} ions. Fourthly, the improved physisorption of the Cd\textsuperscript{2+} ions by BT/ZnO photocatalysts compared with that of pure BT and ZnO could accelerate the photodegradation reaction. Furthermore, the electrostatic interaction of the negatively charged BT can promote the separation of electrons and holes and thus suppresses the charge recombination. It is a fact that ZnO can be activated under UV light source and the valence band (VB) electrons (e\textsuperscript{−}) of ZnO can be easily excited to the CB, inducing the formation of holes (h\textsuperscript{+}) in the VB. The electrons—holes have no opportunity to transfer to BT and should still be present on the ZnO surface. The ZnO-excited electrons and holes should be driven to migrate efficiently because of electrostatic repulsion between the negatively charged electron and the negatively charged BT and electrostatic attraction between the positively charged hole and the negatively charged BT. Therefore, the probability of electron—hole recombination can be decreased and increased, and more charge carriers are available to increase the photoreduction activity. The holes on the VB of ZnO react with TEOA as the electron donor and anionic BT, and the electrons can be trapped by the available surface of O\textsubscript{2} to initiate the yield of reactive species such as anions (O\textsubscript{2})\textsuperscript{−}. The photogenerated electrons and O\textsubscript{2} radicals can effectively reduce Cd\textsuperscript{2+} into nontoxic Cd(0) under UV light irradiation (Figure 7).

**Figure 7.** Proposed mechanism for Cd\textsuperscript{2+} photoreduction over BT/ZnO.
2.4. Langmuir–Hinshelwood Kinetic Study. The photocatalytic reduction of Cd^{2+} over BT/ZnO composites followed the pseudo-first-order kinetics by the following formula

\[ \ln \left( \frac{C_0}{C_t} \right) = -kt \]

In the above equation, \( k \) is the kinetic constant and \( C_0 \) and \( C_t \) are the initial concentration of Cd^{2+} and Cd^{2+} concentration in time \( t \), respectively. The average rate constant (\( k \)) for BT/ZnO composites was found to be 0.086 min^{-1} (Figure 8a), which is larger than those for pure ZnO 0.06 min^{-1} (Figure 8b) and BT 0.053 min^{-1} (Figure 8c). These results revealed that the supporting ZnO-NCs into BT could highly enhance the photoreduction activity under UV light irradiation.

2.5. Analysis of Real Water Samples. The detection and photoreduction of Cd(II) ions were also studied in real water samples including tap and drinking water. Initially, the negligible Cd(II) ion concentration was found to be in the understudy real water samples. Therefore, tap and drinking water samples were spiked with 3.0 mg/L Cd(II) ion concentration, and the photoreduction efficiency was studied to check the applicability of the as-prepared ZnO/BT. The values obtained were found to be 81.02% and 79.85% in the case of tap and drinking water, respectively. Hence, the cycle was repeated for the desorption–adsorption process until consecutively seven cycles were obtained. After seven cycles, we got 79.05% as the maximum Cd(II) photoreduction, which showed satisfactory reusability and stability of the as-prepared photocatalyst. By comparing the FESEM–energy-dispersive spectroscopy (EDS) results of the fresh and recovered photocatalysts, it can be observed that all the elements in the fresh catalyst are also present in the recovered catalyst, indicating the stability of the ZnO/BT structure during the reaction (Figure 9). In addition, the FESEM analysis confirmed that the ZnO/BT morphology was satisfactorily stable during the photoreduction and recovery process (Figure 9).

3. CONCLUSIONS

Photoreduction of Cd(II) was successfully achieved under UV light using ZnO supported on the BT photocatalyst. Using ZnO supported onto the BT clay, the band gap reduced, and the UV light activity was seen for Cd(II) photoreduction. ZnO was excited under UV radiation, and electrons were injected into the CB of BT, which then reduced Cd(II) to Cd(0). We found that different factors such as photocatalyst dosage, Cd(II) concentration, contact time, pH, temperature, and light intensity significantly influenced the photoreduction efficiency.
The results of this research clearly demonstrate the effective role of ZnO/BT in photoreduction via increasing the contact surface between the photocatalyst and Cd(II), making it a suitable choice for the purification of toxic cadmium-containing hazardous wastes, which may lead to cancer. Moreover, ZnO/BT is very suitable and efficient for industrial wastes because of its high ability in the photoreduction of high-concentration contaminants.

4. MATERIALS AND METHODS

4.1. Materials and Instruments. BT with a particle size of 2 μm was provided by Iran Bentonite Co. Caustic soda with a molecular weight of 39.9971 g/mole and 30 wt % concentration and hydrochloric acid with 38 wt % concentration were supplied by Sudparak Iranian Co. and Acid Sazan Zanjani Co., Iran, respectively. The used apparatus includes an XRD spectrometer (Shimadzu model 1800, Japan, pH-meter 780 Metrohm, Switzerland), a scanning electron microscope (VP 1450, LEO-Germany Co.), and an atomic absorption spectrometer (Varian Spectra AA 220FS, Varian Spectra, USA).

4.2. BT Preparation. The as-received BT (300 g) was passed through a filter (200 mesh), followed by washing three times with distilled water and then dispersed and kept in 250 mL of distilled water for 24 h. The suspension was separated under vacuum using a filter paper, and the resultant cake was dried at 25 °C.

4.3. Preparation of BT-Supported Zinc Oxide. First, 2 g of zinc acetate dihydrate was dissolved in 250 mg of ethanol in an ultrasonic bath (60 W) for 3 h to form a homogeneous solution. After that, 10 g of dry BT powder and 100 mL of 30 wt % caustic soda were added to the above solution and stirrerd for 1 h. The mixture was centrifuged, and the resultant precipitate was washed with 300 mL of methanol and centrifuged twice, followed by drying in a vacuum oven at 75 °C. The powder was annealed in a furnace at 200 °C for 2 h.

4.4. Cd(II) Ion Physisorption/Reduction Process. The Cd²⁺ ion photoreduction phenomenon onto the ZnO/BT photocatalyst was performed in a batch process with a flat window at the top under UV light illumination with a 320 nm wavelength in different powers (0−200 W) (Figure 11). ZnO/BT was placed into an Erlenmeyer flask containing 50 mL of Cd(II) ion in an aqueous TEOA solution, and the suspension was stirred at 80 rpm and 40 °C for different times under nitrogen gas purging. The pH solutions were adjusted by HCl and NaOH 0.1 M. Finally, the resultant mixture was centrifuged, and the residual of the Cd(II) ion in the filtrated solution was analyzed by an atomic absorption spectrometer. The removal percentage of the Cd(II) ion was calculated according to the previously reported literature. The optimum conditions for obtaining the best photoreduction/removal efficiency were evaluated, and the effects of various processing parameters were investigated. The mechanism of Cd(II) ion physisorption onto the ZnO/BT photocatalyst is shown in Figure 11.

All steps for the illustration of ZnO/BT preparation and Cd(II) ion physisorption are shown in Figure 10.

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Notes
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