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Selective Removal of Heavy Metals from Drinking Water Using Titanium Dioxide Nanowire

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Summary: Heavy metal contamination in drinking water has become an ecotoxicological hazard of prime interest. Conventional treatment technologies, such as chemical precipitation, coagulation and ion-exchange, are often restricted because of some technical or economic constraints. In view of this, the search for a more innovative and effective adsorbent for the removal of toxic metal ions has intensified in recent years. In this study a novel adsorbent, titanium dioxide nanowire (TiO_2), is prepared by using hydrothermal methods and subsequently used for heavy metal removal. This study tests the potential of using the TiO_2 nanowire to remove heavy metal (Pb^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+} and Zn^{2+}) residues from contaminated water. TiO_2 nanowire is an exceptional adsorbent material due to its magnetic properties and a good adsorption capacity. The highest absorption efficiency was 97.06% obtained with Pb^{2+} and the lowest was obtained with Zn^{2+} at 35.18%. The application of these materials in water filters may be a promising and economically feasible technology for water purification.

Keywords: heavy metal; TiO_2 nanowire; toxic metal ions; water purification

Introduction

Environmental pollution is currently one of the most important issues facing humanity. Heavy metals are toxic contaminants that must be removed from wastewater before discharged to the environment. At trace level, many of these elements are necessary to support life. However, at elevated levels they become a significant health hazard. These harmful materials should be removed from the environment[1] (ATSDR, 2000). Among the class of heavy metals that are classified by the environmental protection agency (EPA), the agency for toxic substances and the disease registry, the top priority for removal of heavy metals from water, are lead (Pb^{2+}), cadmium (Cd^{2+}) and zinc (Zn^{2+}).[2] An increasing demand for the use of ultra-pure water by various industries such as pharmaceutical, electroplating, and semiconductor manufacturing industries has led to the development of modern techniques that are capable of solving the problem of contamination of water by heavy metals.[3] A wide range of physical and chemical processes are available for the removal of heavy metal ions during wastewater treatment. Activated carbon, oxide minerals, polymer materials, resins and biosorbents have been applied as adsorbents to remove metal ions. The adsorption efficiency of these materials depends on the functional groups on the adsorbent surface.[3] Nanomaterials are beginning to show many advantages, especially in environmental sciences. Nanomaterials exhibit novel physical and chemical properties that may not be observed at bulk sizes. Surface, magnetic, and optical properties may change due to decreasing size, different structures, and new methods of nanomaterials synthesis. There are many potential advantages of using nanoparticles for adsorption. The primary advantage is

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the larger and more controllable surface area. In the last decade, the photocatalytic property of TiO_2 has attracted much attention and has been widely studied for its utilizations in the environmental field. For example, TiO_2 has been developed and used as a photocatalyst for indoor and outdoor air purification and for the remediation of contaminated water loaded with low concentrations of toxic organic pollutants.[4] Its application in photocatalytic degradation of organics, such as azo dyes, chlorophenol and phenol, in wastewater has extensively been studied by many researchers.[5,6] However, its use for removing toxic metals from water has only recently been discussed by several authors.[7,8] Most of the researchers investigated the removal abilities of TiO_2 on heavy metals by a well-known commercial TiO_2 product, Degussa-P25. It is a mixed phase titania photocatalyst consisting approximately 80% anatase and 20% rutile. In addition, a new class of nanosized large pore titanium silicate adsorbent with a TiO_2/SiO_2 ratio of 1/5.5 was developed by Choi et al. (2006).[9] TiO_2 nanoparticles are frequently used widely in many applications because of their unique electrical and optic properties as well as extensive application in diverse areas ranging from, self cleaning,[10] anticorrosion[11] coatings,[12] and paints to solar cells. Various properties of TiO_2 nanoparticles are dependent on their crystal sizes, morphologies, and crystallographic structures.[13,14] Hydrothermal methods provide an easy route to prepare a well-crystallized and phase-pure oxide in one step in a tightly closed vessel.[15,16] The hydrothermal preparation of TiO_2 has been examined for several decades. Under various hydrothermal conditions, products of TiO_2 with different morphologies and structural forms, such as rutile, anatase, or even brookite, have been yielded.[17–22] The influence of temperature, pH value, and additives on crystallization of TiO_2 has been reported in several publications in the 1970s.[23–25] In this work we used (TiO_2) nanoparticles (P_{25}) as a precursor for the hydrothermal preparation method for the production titanium dioxide nanowires. This work presents the first report for the using of TiO_2 nanowires for water treatment.

Materials and Methods

Materials

Titanium dioxide (P25, Degussa), with about 30 nm cross-sectional dimension, was used as received. Sodium hydroxide (NaOH) and sodium chloride (NaCl) were used as received from Alfa Aesar and all other organic solvents used in this study were of analytical grade and used without further purification. Stock Standard solution of Zn^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+} and Cd^{2+} were obtained from Merck in concentration of 1000 mg/l (Merck, Darmstadt, Germany. Before use all, the glassware had been soaked in detergent, rinsed with water, soaked in 15% nitric acid, rinsed with distill water and kept in the oven at 110 °C till need.

Methods

In a standard synthesis, 0.2 g of titanium nanoparticales (P25) in aqueous solution of NaOH (10M, 40ml) was placed into a Teflon-lined autoclave.[26] The mixture of titanium dioxide nanoparticales and strong alkaline aqueous medium of NaOH was stirred to form a suspension solution (which is milky in appearance), sealed and hydrothermally treated at 220–260 °C for more than two days. The precipitate formed was separated by filtration and washed with de-ionized water until a pH value near 8 was reached. Up to this stage, the precipitate was in the denoted hydrogen form $Na_xH_{2x}Ti_3O_7$ ($x = 0.75$). Immediately after precipitation, the precipitate was oven-dried at 80 °C for more than 4 h. It should be stressed that the key factor for producing pure TiO_2 nanowires is the optimization of the NaOH concentration as well as the time of hydrothermal treatment.

Characterization

Powder XRD was performed on a Rigaku, Miniflex X-ray diffractometer ME 14848DO4 with CuKα radiation source ($\lambda = 1.5418$ Å).

The lattice spacing was calculated via Bragg's equation. The microstructure of the TiO_2 nanowires was examined for very dilute suspensions of the corresponding nanowires in water using JEOL JEM-1230 transmission electron microscope (TEM) with a Cd^{2+} acceleration voltage of 80 kV. The microscopy samples of the nanowires was prepared by adding a small drop of the water dispersions onto a Lacey carbon film-coated copper grid then allowing them to dry in air. Scanning electron microscope (SEM), Tescan VEGA-II, USA, operated at 20 kV, was used for examining the nanowires morphologies and its surface characteristics. Quantitative determination of Zn^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+} and Cd^{2+} were conducted by using atomic absorption spectrometry. The thermo atomic absorption spectrometer with hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air-acetylene flame. Calibration standards were regularly performed to evaluate the accuracy of the analytical method. Working calibration standards of Zn, Cu, Pb, Fe and Cd were prepared by serial dilution of concentrated stock solution.

TiO_2 nanowire adsorbent was used to determine their efficiency in the removal of toxic heavy metals from artificial wastewater by a column elution technique. A glass column (30 cm x 1.8 cm) were taken and plugged with cotton. TiO_2 nanowires (1 g) were loaded into the column, and were washed with 25 ml distilled water. Water samples (100 ml) were fortified Zn^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+} and Cd^{2+} at 5 mgL^{-1} level and passed through the column. The flow rate was adjusted to 5ml min^{-1}. The eluent was collected in a beaker. 10 ml fractions were taken and the metals determined by atomic absorption spectrophotometry. In addition, blank samples with the metal ions in aqueous solution without adsorbent were simultaneously processed to determine the metals absorption during the recovery process. The removal efficiency of adsorbent was calculated by eliminating the contribution due to processing.

Result and Discussion

To confirm the structure of the prepared nanomaterials, the powder XRD pattern of the TiO_2 nanowires was recorded. After the involvement of P25 in the alkaline hydrothermal reaction, a crystalline structure illustrated as hydrogen from the nanowires and represented as $H_2Ti_3O_7$ was observed. In addition, the XRD of TiO_2 nanowires (Figure 1b) was indexed to the sodium titanate ($Na_2Ti_2O_4(OH)_2$), which has the body-centered orthorhombic crystal structure shown above the corresponding XRD. The body-centered orthorhombic $Na_2Ti_2O_4$

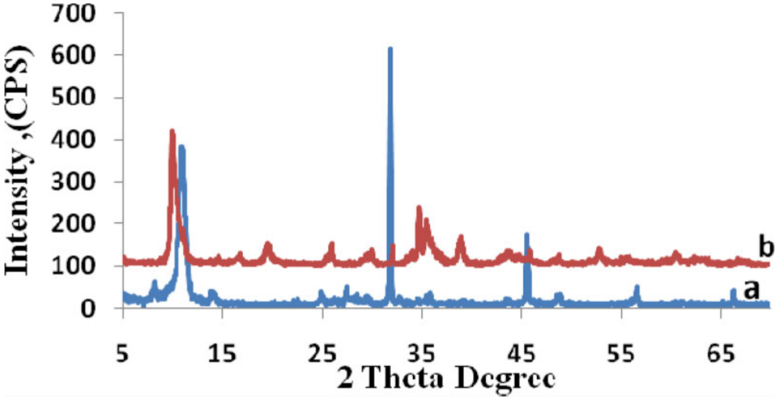

Figure 1.
XRD of TiO_2 nanowires prepared *via* hydrothermal methods a) H- form, b) Na-form.

$(OH)_2$ consists of TiO_6 octahedral structures that share edges to form two dimensional sheets. These sheets are held together and electrostatically stabilized with Na^+ and OH^- in between the layers. Conversely, the peak of diffraction of TiO_2 nanowires appears at $2\theta = 11°$ (d = 8.1 Å), $2\ \theta = 31°$ (d = 3 Å) and $2\ \theta = 45.5°$ (d = 2.16 Å).

Moreover, Figure 1 clearly shows a slight shift of this multilayered crystalline structure with lattice spacing expanding from 0.73 nm for the hydrogen to 0.96 nm after the completion of the ion exchange process.

The Figure 2 illustrates the formation of TiO_2 nanowires by SEM analysis. These results established that the nanowires which formed by the hydrothermal process using very strong alkaline medium of 10 M NaOH and rinsing the white produce materials by water till pH equal 8, remain stable. Moreover, the Na-form nanowire's morphology was characterized the SEM and shows well-grown Na-nanowires. The TiO_2 nanowires are apparent in the SEM image as wires with a smooth surface each with an average length >10 μm and an average diameter 30–50 nm. Most of the TiO_2 nanowires are well-separated single wires even though some occur in aggregated bundles, all of which nonetheless possess a smooth surface which is typical for a single crystalline structure. This supports the data shown in Figure 1.

Supplementary examination of any probable associated surface modifications throughout hydrothermal treatment step of P_{25} using 10 M NaOH at high temperature was followed with TEM images taken at different magnifications (Figure 3). From Figure 3, it is clear that there is a diffraction contrast around the edges which clearly proves that the attained nanostructures are typically nanowires. The inner diameter was in the range of 750 nm while the outer diameter of the nanowires was around 24 nm, with the tendency of the nanowires to twin together or exist in groups. Further, TEM was used to confirm that the nanowire axis was definitely in the [100] direction by measuring the angle between the {101} planes of anatase and the local nanowire axis. In addition, after modified nanowires were prepared by using 2 M NaCl to exchange H^+ by Na^+ as evidence by XRD patterns in Figure 1., demonstrates the change in the nanostructure of sodium form.

As mentioned previously, the removal of heavy metals has become a primary goal for

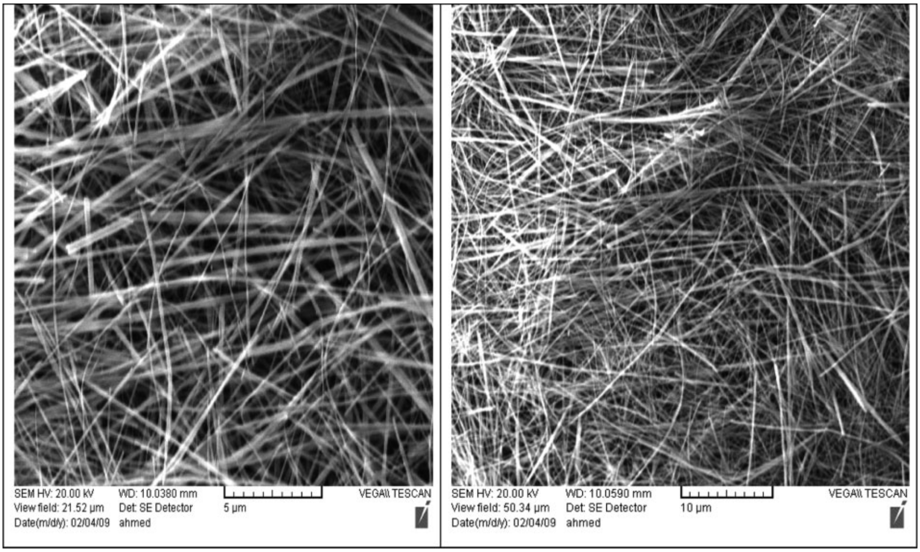

Figure 2.
Scanning electron microscope SEM image of TiO_2 nanowires.

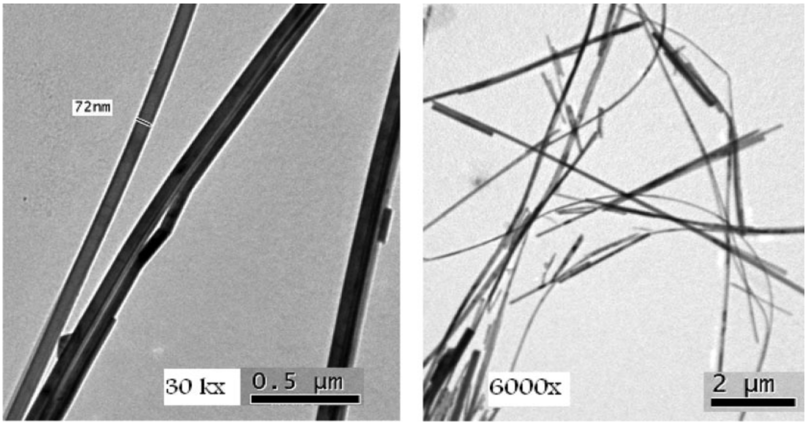

Figure 3.
Transmission electron microscope TEM image of TiO_2 nanowires prepared through hydrothermal treatment as a white precipitation taken from the 10M NaOH solution and dispersed in acetone solution.

obtaining clean water resources and non-threatening wastewater. Due to their good absorption efficiency, TiO_2 nanowires were used in this study to absorb the toxic heavy metal from water. It was observed from the comparison of the initial and final concentration of the water samples that the TiO_2 nanowires exhibited different affinities for the different metals (Table 1).

The absorption experiments were performed by means of a simple column setup and direct determination of the metal concentration by atomic absorption spectrophotometer. The initial concentration of the metal in water in this study refers to the concentration of a sample without treatment. The highest absorption efficiency was 97.06% obtained with Pb^{+2} and the lowest was obtained with Zn^{+2} at 35.18%. The results suggested that TiO_2 nanowires have a stronger adsorption affinity for Pb^{+2} than Cd^{+2} and Zn^{+2} ions. This phenomenon is in agreement with the finding of Kabra et al. (2007).[8] They found that TiO_2 is ineffective for Zn^{2+} removal from water at pH 7 compared with Pb^{2+}. Also, the results indicated that the performance of this novel adsorbent on heavy metal removal is quite promising, especially in the application of Pb^{2+}, Cd^{2+} and Cu^{2+} purification. The application of these materials in water filter may be a promising and economically feasible technology for water purification.

Table 1.
Efficiency of TiO_2 nanowires for removal of heavy metals residues from water.

Heavy Metal	Conc. before absorption (mg/L)	Conc. after absorption (mg/L)	Removal %
Pb^{2+}	5.00	0.14	97.06
Cu^{2+}	4.72	2.20	75.24
Zn^{2+}	4.27	2.77	35.18
Cd^{2+}	4.48	2.47	64.89
Fe^{3+}	4.39	1.19	79.77

(The values in table 1 reported for average for a series of experiments).

Conclusion

Titanium dioxide nanowire (TiO_2), were prepared by using the hydrothermal method and subsequently used for water purification by removing heavy metal ions. Heavy metals were removed from contaminated water by using TiO_2 nanowire as adsorbent material owing to its magnetic properties and a good adsorption capacity. The absorption efficiency of TiO_2 nanowires towards different heavy metals (Pb^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+} and Zn^{2+} was 97.06, 75.24, 79.77, 64.89 and 35.18% respectively). These materials may be used as part of a water purification filter and can also be considered as a promising and economically feasible technology for ground water treatment.

[1] ATSDR **2000**. Toxicological profile for chromium on CD-ROM. Agency for Toxic Substances and Disease Registry. U.S. Public Health Service.

[2] ATSDR **2003**. ToxFAQs, ATSDR Toxicological profiles and public health statements, http://www.atsdr.cdc.gov/toxfaq.html.

[3] A. M. Youssef, F. M. Malhat, A. A. Abd El-Hakim, *Polymer-Plastics Technology and Engineering*, **2013**, *52*, 228.

[4] G. Li Puma, A. Bono, D. Krishnaiah, Collin, *Journal of Hazard Materials*, **2008**, *157*, 209.

[5] M. Antonious, D. Dionysiou, *Catalysis Today*, **2007**, *124*, 215.

[6] Y. Ku, Y. Lee, W. Wang, *Journal of Hazard Materials*, **2006**, *138*, 350.

[7] A. Barakat, *J Colloid and Interface Science*, **2005**, *291*, 345.

[8] K. Kabra, R. Chaudhary, R. Sawhney, *Journal of Hazard Materials*, **2007**, *149*, 680.

[9] J. H. Choi, S. D. Kim, Y. J. Kwon, W. J. Kim, *Microporous and Mesoporous Materials*, **2006**, *96*, 157.

[10] A. A. Hebeish, M. M. Abdelhady, A. M. Youssef, *Carbohydrate Polymers*, **2013**, *91*, 549.

[11] W. C. Liaw, K. P. Chen, *European Polymer Journal*, **2007**, *43*, 2265.

[12] A. L. Linsebigler, G. O. Lu, J. I. Yates, *Chem Rev*, **1995**, *95*, 735.

[13] H. Zhang, J. F. Banfield, *Journal of Material Chemistry*, **1988**, *8*, 2073.

[14] R. L. Penn, J. F. Banfield, *Mineral*, **1988**, *83*, 1077.

[15] T. Adschiri, K. Kanazawa, K. Arai, *Journal of the American Ceramic Society*, **1992**, *75*, 1019–1022.

[16] Y. T. Qian, Q. W. Chen, Z. Y. Chen, C. G. Fan, G. E. Zhou, *Journal of Material Chemistry*, **1993**, *3*, 203.

[17] C. C. Wang, J. Y. Ying, *Chemistry Material*, **1999**, *11*, 3113.

[18] M. M. Wu, J. M. Long, A. H. Huang, Y. J. Luo, S. H. Feng, R. R. Xu, *Langmuir*, **1999**, *15*, 8822.

[19] K. Yanagisawa, J. Ovenstone, *Journal of Physical Chemistry B*, **1999**, *103*, 7781.

[20] R. Bacsa, M. Gratzel, *Journal of the American Ceramic Society*, **1996**, *79*, 2185.

[21] T. Sugimoto, K. Okada, H. Itoh, *Journal of Colloid Interface Science*, **1997**, *193*, 140.

[22] H. M. Cheng, J. M. Ma, Z. G. Zhao, L. M. Qi, *Chemistry Material*, **1995**, *7*, 663.

[23] F. Izumi, Y. Fujiki, *Bulletin of the Chemical Society of Japan*, **1976**, *49*, 709.

[24] F. Izumi, *Bulletin of the Chemical Society of Japan*, **1978**, *51*, 1771.

[25] E. Matijevic, *Journal of Colloid Interface Science*, **1977**, *58*, 374.

[26] A. A. Haroun, A. M. Youssef, *Synthetic Metals*, **2011**, *161*, 2063.