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Study of cyanide removal from contaminated water using zinc peroxide nanomaterial

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ABSTRACT

The present study highlights the potential application of zinc peroxide (ZnO_2) nanomaterial as an efficient material for the decontamination of cyanide from contaminated water. A process patent for ZnO_2 synthesis has been granted in United States of America (US Patent number 8,715,612; May 2014), South Africa, Bangladesh, and India. The ZnO_2 nanomaterial was capped with polyvinylpyrrolidone (PVP) to control the particle size. The PVP capped ZnO_2 nanomaterial (PVP-ZnO_2) before and after adsorption of cyanide was characterized by scanning electron microscope, transmission electron microscope, X-ray diffractometer, Fourier transform infrared spectroscopy and time of flight-secondary ion mass spectrometry. The remaining concentration of cyanide after adsorption by PVP-ZnO_2 was determined using ion chromatograph. The adsorption of cyanide over PVP-ZnO_2 was also studied as a function of pH, adsorbent dose, time and concentration of cyanide. The maximum removal of cyanide was observed in pH range 5.8–7.8 within 15 min. The adsorption data was fitted to Langmuir and Fruendlich isotherm and it has been observed that data follows both the isotherms and also follows second order kinetics.

Introduction

Cyanide is one of the anthropogenic contaminant in natural water through several industrial effluents and considered as highly toxic for aquatic life and human beings. It enters human body through inhalation, ingestion, absorption through skin, eyes, and mucous membranes. Industrial exposure even for short term can cause tremors and neurological disorder, while long term exposure causes weight loss, thyroid dysfunction and nerve damage and hypoxia. It stimulates the chemoreceptor of the carotid and aortic bodies, causing hyperpnoea (Tiwari et al., 2007). Approximately 14 million kg per year of cyanide from industries worldwide is released into environment (Ebbs, 2004). Out of this, 13% cyanide is used for the extraction of gold and silver. However 87% of cyanide is used in production of paint, adhesives, electroplating (Gallerani and Drake, 1993), computer electronics, metal refining (Akcil, 2003), chemical manufacturing, steel tempering (Saxena et al., 2001), dyes, nylon, petrochemical applications, photography industry, rocket propellant, pharmaceuticals, coal carbonization (Dash et al., 2009) *etc.* Sodium cyanide form is mainly used in mining industry for extraction of precious metals like gold and silver (Sharma et al., 1998). The mining, electroplating, coal, and pharmaceutical related industries generate maximum cyanide (Parga et al., 2009; Shirzad Siboni et al., 2011). Cyanide is naturally produced by both fauna and flora. It is also found in -SCN form in human

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urine (<0.007 g/L) and gastric juice (<0.006 g/L). Since 1930 it is being used for various applications in medicine, esthetics, firework, and surgical infections (Meleney, 1941). It is also one of the parts of codeine, cocaine, morphine, and caffeine drugs. Worldwide various countries have set their threshold limits for cyanide, like 0.1 mg/L in Argentina, South Africa and Germany, 1.5 mg/L in Mexico, 50 mg/L in Australia. World Health Organization (WHO) has set a limit of 0.07 mg/L of hydrogen cyanide (WHO, 2011), whereas United State-Environmental Protection Agency (US-EPA) has set 0.2 mg/L as maximum contaminant limits (MCL) of cyanide for safe level of drinking water. So in order to protect wildlife, nature and human beings it is absolutely essential to remove or neutralize prior to discharge. In literature several methods are reported for removal of cyanide from water such as alkaline chlorination (Mapstone and Thorn, 1978), oxidation with ozone, hydrogen peroxide, sulfur dioxide (Kepa et al., 2008), ion exchange (Song et al., 2005), photocatalytic degradation (Karunakaran et al., 2011), adsorption (ROSHAN et al., 2006), biodegradation (White et al., 2000) and acidification volatilization recovery (AVR). Photocatalytic degradations of cyanide have been done using different materials like ZnO, TiO_2, and CeO_2. In addition to these, several organic and inorganic adsorbents like pure and metal impregnated activated carbon, coal, charcoal, zeolites, alumina and agricultural by products have also been reported for removal of cyanide.

The above processes and materials have their own limitations for cyanide removal like oxidation causes formation of toxic hypochlorite and other chlorinated byproducts. Alkaline chlorination process forms cyanogen chloride, which is highly toxic and create additional environmental problem. AVR technique requires optimization of pH and generates acutely toxic gas hydrogen cyanide and also required sealed vessels and packed columns. Ion exchange process is expensive, time consuming and produce harmful byproducts. The photocatalytic degradations require ultraviolet light. Activated carbon compounds are comparatively expensive and difficult to regenerate, while zeolites and agricultural by products are relatively less expensive but having less capacity to remove cyanide. However adsorption is most preferable being a simple, efficient and economical process. Still there is a growing need for alternative method for the removal of cyanides. In this context, we have synthesized polyvinylpyrrolidone (PVP) capped ZnO_2 nanomaterial (PVP-ZnO_2), which is nontoxic, efficient, easy to synthesize and does not require expensive chemicals and sophisticated instrumentation. The PVP-ZnO_2 removes cyanide from contaminated water through combined effect of electrophilic addition mechanism and electrostatic interaction and makes water usable for several household applications.

1. Experimental

1.1. Equipment and chemicals

The chemicals used for the synthesis of PVP-ZnO_2 and cyanide determination like zinc acetate, ammonia, sodium hydroxide, hydrogen peroxide, hydrochloric acid, PVP, and methanol were of analytical grade and procured from E. Merck India. High purity de-ionized water (18.2 MΩ cm resistivity; 0.22 μm filtered, metallic impurities at ng/kg level) was obtained from Millipore milli-Q element water purification system procured from USA. The cyanide removal experiments were carried out using cyanide reference standard solution of 1000 ± 10 mg/L (traceable to NIST SRM 1.19533, $K_2[Zn(CN)_4]$ in H_2O) procured from Merck Germany after subsequent dilutions in de-ionized water. The remaining concentrations of cyanide after adsorption were determined by ion chromatograph (IC 850 Metrohm using SUP-100 detector and 4% sodium hydroxide solution as carrier). The pipettes, beakers, volumetric flasks used were of Borosil Glass Works India Limited and were calibrated prior to analysis by CSIR-National Physical Laboratory-India (National Metrology Institute of India) following international standard procedure and protocol.

1.2. Synthesis of PVP-ZnO_2

For the synthesis of PVP-ZnO_2, 10 g of zinc acetate was dissolved in 200 mL of 10% ammonium hydroxide solution (pH 10–11). The solution was diluted to 400 mL by methanol water mixture (water:solvent, 4:1, *V/V*). To this solution, 1 g PVP was added and mixed thoroughly on magnetic stirrer at constant temperature (50–55°C) and speed (around 500 rounds/min). Further 50 mL of 25% hydrogen peroxide solution was added to each solution with continuous stirring. White precipitate formed which was then centrifuged at 10,000 rounds/min and washed thoroughly with de-ionized water and finally dried at 105°C. The details of synthesis process are given elsewhere, in which we have claimed synthesis process of nanosize ZnO_2 particles using different capping agents (Singh Nahar et al., 2014).

1.3. Determination of point of zero charge

The point of zero charge (pH_{pzc}) corresponds to pH where net charge over surface of adsorbent is zero. The surface of adsorbent is considered as positively charged when it adsorbs at pH below its pH_{pzc} and negatively charged when it adsorbs above pH_{pzc}. The pH_{pzc} of PVP-ZnO_2 was determined by mass potentiometric titration method (Bourikas et al., 2003; Mahmood et al., 2011) in which two similar solutions of sample and blank were prepared in 0.03 mol/L KNO_3 and allowed to stir for 24 hr to stabilize pH. Then 1 mol/L KOH was added to deprotonate the surface sites and 0.05 mL of 0.1 mol/L HNO_3 was added subsequently using a micropipette and pH was noted after each addition of HNO_3. The obtained pH values for both sample and blank were plotted against volume of HNO_3. The common point of intersection between sample and blank was appeared at pH 7.9 as shown in Fig. 1 which has been considered as pH_{pzc} of PVP-ZnO_2.

1.4. Characterization

The synthesized PVP-ZnO_2 was characterized for its phases by an X-ray diffractometer (XRD, Bruker, model AXS D8 Advance Diffractometer). The diffractogram was recorded using CuKα radiation source with graphite monochromator in the diffracted beam. The shape and size of PVP-ZnO_2 before and after cyanide adsorption were characterized using a Transmission Electron Microscope (TEM, FEI, model F-30 G2 STWIN, Netherland)

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