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 (ZnO2) nanomaterial as an efficient material for the decontamination of cyanide from contaminated water. A process patent for ZnO2 synthesis has been granted in United States of America (US Patent number 8,715,612; May 2014), South Africa, Bangladesh, and India. The ZnO2 nanomaterial was capped with polyvinylpyrrolidone (PVP) to control the particle size. The PVP capped ZnO2 nanomaterial (PVP-ZnO2) 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-ZnO2 was determined using ion chromatograph. The adsorption of cyanide over PVP-ZnO2 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 Freundlich isotherm and it has been observed that data follows both the isotherms and also follows second order kinetics.

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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 Thiocyanate anion...
(−SCN) form in human 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, TiO₂, and CeO₂. 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 preferably 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 ZnO₂ nanomaterial (PVP-ZnO₂), which is nontoxic, efficient, easy to synthesize and does not require expensive chemicals and sophisticated instrumentation. The PVP-ZnO₂ 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-ZnO₂ 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, K₂[Zn(CN)₄] in H₂O) 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-ZnO₂

For the synthesis of PVP-ZnO₂, 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 ZnO₂ 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-ZnO₂ 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 KNO₃ 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 HNO₃ was added subsequently using a micropipette and pH was noted after each addition of HNO₃. The obtained pH values for both sample and blank were plotted against volume of HNO₃. 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-ZnO₂.

1.4. Characterization

The synthesized PVP-ZnO₂ 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-ZnO₂ before and after cyanide adsorption were characterized using a Transmission Electron Microscope (TEM, FEI, model F-30 G2 STWIN, Netherland)
where,

\[ q_e = \frac{(C_i - C_f) \times V}{m} \]  

and

\[ R = \left( \frac{C_i - C_f}{C_i} \right) \times 100\% \]

1.5. Adsorption study

The synthesized PVP-ZnO₂ was tested initially for 25 mL of 2 mg/L cyanide solution. The pH of test solution was adjusted around 7.0 and 250 mg of PVP-ZnO₂ was added to it and kept for 30 min. The decanted solution was then tested for leftover concentration of cyanide. The adsorption capacity \( q_e \) of PVP-ZnO₂ for cyanide removal and removal of cyanide \( R, \% \) was calculated by Eqs. (1) and (2) respectively.

The elemental mapping of PVP-ZnO₂ before and after cyanide adsorption are shown in Fig. 5a and b, respectively. The spectrum clearly indicates the presence of C, O, cyanide (CN⁻) and Zn. In Fig. 5a the peaks of C and O are more intense at negative mode due to their electronegative nature, however intense peak of Zn is observed at positive mode. Similarly in mass spectra of PVP-ZnO₂ after cyanide adsorption as presented in Fig. 5b, an intense peak CN⁻ along with C and O has been observed at negative mode, whereas intense peak of Zn has been observed at positive mode.

2. Results and discussion

2.1. Characterization

The PVP-ZnO₂ has been characterized for its phases and crystallite size by XRD. The spectrum was recorded in 2θ range from 20 to 80° and has been presented in Fig. 2a. The crystallite size of PVP-ZnO₂ calculated from Scherer’s equation (Cullity and Stock, 2001) was found to be 12 ± 2 nm. The observed diffractions peaks were compared with XRD data PDF # 13-0311, which confirms formation of a single-phase PVP-ZnO₂. The XRD pattern of PVP-ZnO₂ is found to be in good agreement with cubic structure of nano ZnO₂ (Cheng et al., 2009) having (111) plane corresponding to interplanar spacing of 0.278 nm. The size and shape of PVP-ZnO₂ was characterized by TEM. The micrograph obtained has been presented in Fig. 2b. The TEM and EDX studies were carried out after depositing test material over carbon (C) coated copper (Cu) grid of 200 mesh size. The TEM micrograph indicates that the material is composed of nanoparticles with diameters of 10–15 nm. The material shows agglomerated nature, however individual particle shows distinct boundary. The shape of the particles was found to be spherical as depicted in same image. The presence of Cu is also correlated to pyrrolidone groups of PVP, however N has not been observed in the same EDX. This might be due to use of smaller amount of PVP used for controlling size of ZnO₂ particles or concentration of N may be below detection limit of EDS system.

The PVP-ZnO₂ nanomaterial after adsorption of cyanide was filtered and dried at 105°C. The TEM micrograph of cyanide adsorbed PVP-ZnO₂ indicates highly agglomerated ZnO₂ nanoparticles, which may be due the adsorption of cyanide over the particles (Fig. 3a). The EDX spectra and elemental composition indicate the presence of N along with Zn, O, C and Cu (Fig. 3b and c). The presence of N has been correlated to cyanide.

FT-IR spectra of PVP-ZnO₂ before and after cyanide adsorption were measured at room temperature in the spectral range of 4000–400/cm as shown in Fig. 4. The spectrum shows a characteristic peak at 1070/cm arise from the O–H stretching vibration of water. These bands indicate the presence of small amount of water adsorbed on the surface of ZnO₂. In addition, the band at 1380/cm has been observed in the case of PVP-ZnO₂ after cyanide removal, which is due to C–N stretch.

The TOF-SIMS experiments for the compositional analysis of PVP-ZnO₂ before and after cyanide adsorption have also been carried out. The spectra were taken to identify the elements and molecules present on both samples at positive and negative modes. The spectra of PVP-ZnO₂ before and after cyanide adsorption are shown in Fig. 5a and b, respectively. The spectrum clearly indicates the presence of C, O, cyanide (CN⁻) and Zn.
From the elemental mapping of PVP-ZnO$_2$, it was clearly observed that distribution of Zn over the sample is more prominent (brighter) in positive mode whereas C and O are clearer in negative modes as given in Fig. 6a. Similarly elemental mapping of PVP-ZnO$_2$ after cyanide adsorption was also done at positive and negative modes. Fig. 6b shows intense peak of Zn at positive modes, whereas intense peaks of C, O and CN$^{-}$ were observed at negative modes The distribution of Zn in PVP-ZnO$_2$ at positive mode as presented in Fig. 6a seems to be stripe like order, whereas after cyanide adsorption as given in Fig. 6b, it changes to irregular order.

2.2. Optimization of pH, adsorbent dose, contact time and concentration of adsorbate on cyanide removal

The pH of the solution for maximum adsorption of adsorbate and pH$^{\text{pzc}}$ of adsorbent have significant effect on adsorption. The pH controls the charge over adsorbent as well as adsorbate. For pH optimization, 8 sets having 50 mL of 2 mg/L cyanide solution were taken separately. The pH of each set was adjusted within range 2–10 with the help of 0.001 mol/L solution of hydrochloric acid or sodium hydroxide. To each beaker 0.1 g of PVP-ZnO$_2$ nanomaterial was added and allowed to ultrasonicate for 2–3 min. Each set was kept for 30 min at room temperature for adsorption. The mixture in each set was then subjected to centrifuge for 2–3 min at 7000–8000 r/min to separate cyanide adsorbed PVP-ZnO$_2$ from water. Finally each decanted solution was analyzed for remaining cyanide concentration. The result of pH variation versus removal of cyanide has been presented in Fig. 7a. It has been found that maximum adsorption of cyanide occurs in pH range 5.8–7.8 which has been considered as optimized pH range for adsorption of cyanide. While on further increasing or decreasing pH of test solution, adsorption capacity of PVP-ZnO$_2$ decreases. The pH$^{\text{pzc}}$ of proposed PVP-ZnO$_2$ was found to be 7.9, which indicates positively charged surface of the PVP-ZnO$_2$ nanomaterial. The positively charged surface thus attracts negatively charged cyanide ions.

After pH optimization, adsorbent dose was optimized by varying the amount of PVP-ZnO$_2$ from 0.025 to 0.5 g for same volume and concentration of cyanide solution. The experimental result for removal efficiency of varying PVP-ZnO$_2$ for cyanide has been presented in Fig. 7b. It was observed that the removal of cyanide increases as the adsorbent dose increases from 0.025 to 0.1 g, due to the increase in active site on the surface of PVP-ZnO$_2$. With increasing adsorbent dose above 0.1 g, the removal percentage of cyanide was found to be unaffected due to overlapping of active sites on the surface of PVP-ZnO$_2$. The maximum percent removal was observed for 0.1 g which was considered as optimized adsorbent dose.

After optimization of pH and adsorbent dose, the removal of cyanide was studied as a function of time at different time intervals (1–30 min) to optimize contact time. The effect of
time on cyanide removal has been presented in Fig. 7c. It has been observed that the removal of cyanide increases with time. The maximum removal of cyanide has been observed in 15 min.

The effect of varying concentration of cyanide (0.5–6.0 mg/L) on cyanide removal by PVP-ZnO₂ was also studied at optimized pH, adsorbent dose and time. The results of cyanide concentration vs. cyanide removal have been presented in Fig. 7d. It has been observed that the cyanide removal decreases from 99.3% to 73.5% with increasing cyanide concentration from 0.5 to 6 mg/L. The decrease in cyanide removal is due to non-availability of active sites with increasing cyanide concentration. It is due to the fact that adsorbent dose is fixed hence active sites of adsorbent are also fixed which gets saturated after adsorption of certain amount of cyanide.

### 2.3. Kinetics study

In order to determine the adsorption process of cyanide on PVP-ZnO₂, pseudo first order and pseudo second order kinetic models were used. The linear pseudo first order and pseudo second order rate equation are represented by Eqs. (3) and (4) respectively.

\[
\ln (q_m - q_t) = \ln q_e - K_1 t 
\]

\[
t/q_t = 1/K_2 q_e^2 + t/q_e 
\]

where, \(q_m\) (mg/g) and \(q_t\) (mg/g) are the amount of cyanide adsorbed at equilibrium and at time \(t\) respectively, \(K_1\) (min⁻¹) is pseudo first order rate constant and \(K_2\) (g/(mg·min)) is the pseudo second order rate constant. For pseudo first order kinetics, a linear curve as presented in Fig. 8a was obtained on plotting \(\ln(q_m - q_t)\) vs. \(t\) (as per Eq. (3)), slope and intercept of which give the value of \(K_1\) and \(q_e\). Similarly for pseudo second
order kinetics (as per Eq. (4)), a linear curve as presented in Fig. 8b was obtained on plotting $t/q_t$ vs. $t$ and slope and intercept of which gives the value of $q_e$ and $K_2$.

The value of $K_1$ calculated from the slope of linear curve as presented in Fig. 8a was found to be 0.135 min$^{-1}$. The value of $q_e$ calculated from intercept of same curve was found to be 0.721 mg/g. whereas $q_e$ calculated from slope of linear curve for second order kinetics as presented in Fig. 8b was found to be 1.106 mg/g and value of $K_2$ calculated from intercept of same curve was found to be 0.29 g/(mg·min). On the basis of correlation coefficient ($R^2$) the adsorption data was best fitted to pseudo second order kinetics. The applicability of second order kinetic indicates chemisorption process.

2.4. Adsorption isotherm analysis

The adsorption isotherm expresses the relationship between amount of adsorbate adsorbed ($q_e$) and equilibrium concentration ($C_f$). The adsorption isotherms are also helpful for describing the interaction between adsorbent and adsorbate by using Langmuir and Freundlich isotherm models. The adsorption data of varying concentration of cyanide adsorbed on PVP-ZnO$_2$ were fitted to Langmuir and Freundlich isotherm models. The Langmuir isotherm suggests the monolayer adsorption on homogenous surface without any interaction between adsorbed ions and is expressed as:

$$C_f/q_e = C_f/q_m + 1/q_mC_L$$  \hspace{1cm} (5)

where, $C_f$ (mg/L) is the equilibrium concentration, $K_L$ (L/mg) is Langmuir constant related to the capacity and energy of adsorption. As per Eq. (5), a linear curve was obtained on plotting $C_f/q_e$ vs. $C_f$ as presented in Fig. 9a. The value of $q_m$ and $K_L$ was calculated from slope and intercept of same curve.

Freundlich adsorption isotherm reveals the multilayer adsorption on the heterogeneous surface of adsorbent and is expressed as:

$$\ln q_e = \ln K_F + 1/n \ln C_f$$  \hspace{1cm} (6)

where $K_F$ (mg/(g·(L/mg)$^{1/n}$)) and $n$ are temperature dependent Freundlich constants related to adsorption capacity and adsorption intensity respectively. As per Eq. (6), on plotting $\ln q_e$ vs. $\ln C_f$, a linear curve was obtained as presented in Fig. 9b. The value of $K_F$ and $n$ was calculated from the slope and intercept of same curve.
a) Polyvinylpyrrolidone capped zinc peroxide

Positive mode

Negative mode

b) Cyanide adsorbed polyvinylpyrrolidone capped zinc peroxide

Positive mode

Negative mode

Fig. 6 – Elemental mapping of (a) polyvinylpyrrolidone capped zinc peroxide and (b) cyanide adsorbed polyvinylpyrrolidone capped zinc peroxide.
Fig. 9 shows that the experimental adsorption data for varying concentration of cyanide follows both Langmuir and Freundlich isotherms on the basis of almost similar value of $R^2$. The $q_m$ calculated from slope of Langmuir isotherm as presented was found to be 2.283 mg/g which is in good agreement with experimental adsorption capacity i.e. 2.205 mg/g. Similarly $K_L$ calculated from intercept of same isotherm was found to be 9.345 L/mg. The value of $n$ obtained from slope of Freundlich isotherm was found to be 2.785. Similarly, $K_F$ obtained from intercept of same isotherm was found to be 2.073 mg/(g·(L/mg)$^{1/n}$).

2.5. Proposed mechanism

The adsorption of cyanide over PVP-ZnO$_2$ is combined effect of PVP and ZnO$_2$. The PVP contains hydrophilic pyrrolidone as well as hydrophobic vinyl group. The PVP acts as capping agent and controls the size of ZnO$_2$ particle through a layer of
coordination bond formed between nitrogen atoms of pyrrolidone (Saravanan et al., 2011). The oxygen in PVP is more electronegative than carbon and it will pull electrons of C–O bond. Due to this effect, the electron density on adjacent carbon decreases and it attracts the electrophilic cyanide groups. However some of cyanide directly interacts with Zn$^{2+}$ ions of ZnO$_2$ through electrostatic interaction. The schematic figure for interaction between PVP-ZnO$_2$ and cyanide (CN$^-$) has been presented in Fig. 10.

2.6. Regeneration and reusability study

The adsorbent is considered to be more economical and feasible if it can be regenerated and use repeatedly for many cycles. In regeneration study, the cyanide loaded PVP-ZnO$_2$ was separated from solution, dried at 105°C and further treated with 0.01 mol/L NaOH solution. The solution was then ultrasonicated for 15 min and the resulting solution was filtered and checked for leached out concentration of cyanide. The filtered PVP-ZnO$_2$ nanomaterial was tested once again for cyanide adsorption following same procedure as earlier study. The same regeneration and reusability process was performed for two more cycles. It was found that the removal efficiency of regenerated PVP-ZnO$_2$ for cyanide was found to be 87% and 76% respectively.

3. Conclusion

A novel application of PVP-ZnO$_2$ nanomaterial has been presented as a potential adsorbent for the removal of cyanide from contaminated water. The solubility of bulk ZnO$_2$ in water is 0.0004% at 17.8°C. In the same way, the solubility of PVP-ZnO$_2$ is very low. The soluble impurities of PVP-ZnO$_2$ nanomaterial was washed out during purification, filtration and washing process. PVP is biocompatible and it can be safely used for water purification after capping on ZnO$_2$ nanomaterial. During adsorption process, the pH of the solution does not alter and there is no need to adjust the pH of water using acid or alkali for functioning of adsorbent. The adsorption process is dependent on pH of water. The maximum efficiency were observed at optimized pH, however the efficiency of cyanide removal alters 5%–10% on increasing (>7.8) or decreasing (<5.8) pH of test water. The decrease in adsorption efficiency is probably due to change in charge of adsorbent and adsorbate on variation of pH. The maximum removal of cyanide was achieved at pH 5.8–7.8 in 15 min. However the cyanide removal efficiency decreases on increasing cyanide concentration with fixed amount of adsorbent. The treated water can be safely used for drinking purposes and others household applications. Beside these the method used for the synthesis of PVP-ZnO$_2$ is very simple, fast, eco-friendly, economical and can be utilized for bulk production of nano size ZnO$_2$. The left over concentration of zinc and acetate ions in the filtrate water was also analyzed using Atomic Absorption Spectrometer and Ion Chromatograph respectively. In each case the concentration of zinc and acetate ions were found below detection limits of AAS and Ion chromatograph. The main reason is that the synthesized PVP-ZnO$_2$ was repeatedly washed several times with solvents like alcohol and DI water.
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