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An Efficient and Fast Process for the Removal of Trivalent and Hexavalent Chromium from Contaminated Water Using Zinc Peroxide Nanomaterial

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Abstract

Higher concentration of trivalent and hexavalent chromium (percent to mg L^{-1}) can be effectively removed from water by adsorption or precipitation process, but difficult to remove lower concentration (<0.25 mg L^{-1}) upto prescribed limits of World Health Organization (WHO) and United State-Environment Protection Agency (US-EPA). The lower concentration of chromium can be effectively removed using reverse osmosis system. In the proposed study we have successfully removed higher to lower concentration (20 to 0.1 mg L^{-1}) of trivalent and hexavalent chromium using alone polyvinylpyrrolidone (PVP) functionalized zinc peroxide (ZnO_2) nanomaterial below detection limit (0.001 mg L^{-1}) of Flame Atomic Absorption Spectrophotometer instrument (FAAS) within 15 minutes. The utilized nanomaterial alone act as oxidizing as well adsorbing agent, and purify water upto safe potability limits. The adsorption capacity of functionalized ZnO_2 nanomaterial for total chromium was found to be 4.98 mg g^{-1} which is much better than the several other materials reported in the literature for chromium removal. A process patent for the synthesis of varying sizes functionalized ZnO_2 nanomaterials has been granted in United State of America (Patent number 8,715,612; May 2014), South Africa, Bangladesh and India.

Keywords: Zinc peroxide; Trivalent and hexavalent chromium; Adsorption mechanism; Langmuir; Freundlich; Dubinin raduskevich isotherms

Introduction

Chromium is a common contaminant in water, largely arising from textile, leather, and wood production industries. Trivalent chromium generally discharges from metal industries, while hexavalent chromium originates from tanning and painting industries. Trivalent chromium helps in insulin secretion in human beings, which remove glucose from blood and also plays a vital role in fat metabolism. On the other hand hexavalent chromium is very toxic to flora and fauna and causes numerous lethal effects on human beings [1-4]**.** The toxic effects of chromium in water are well known and can not be treated by medicine. Hexavalent chromium considered 1000 times more toxic than trivalent chromium. Exposure to hexavalent chromium causes allergy, diarrhoea, intestinal bleeding, cramps, paralysis, liver and kidney damage. Hexavalent chromium is mutagenic and carcinogenic in nature and toxic effects may be passed into children through the placenta. Worldwide efforts have been made to remove chromium from contaminated water up to safe potable limit. The removal of trivalent and hexavalent chromium from contaminated water and make it potable as per WHO and US-EPA standard is a very challenging task. WHO and US-EPA have fixed 50 µg L^{-1} and 100 µg L^{-1} respectively of total chromium in drinking water [5]. Several methods, technologies, and materials used for removal of chromium are ion exchange [6], ultrafiltrartion [7], nanofiltration [8], Microbiological Treatment [9], oxidation [10], fly ash, zero–valent iron [11,12], activated carbon [13,14], Bentonite [15], agricultural wastes [16] washing with hot water [17], microorganisms [18]. However the most common industrial treatment process is based on reduction of hexavalent chromium into trivalent chromium by some reducing agent or by weak acid cation exchange resin followed by precipitation with ferric salt as $Cr(OH)_3$ and finally filtration [19].

So there is a need to develop a low cost, effective process for removal of chromium from water to protect health of people, who are consuming chromium contaminated water. In contuination of prior art as desribed in literature, we have also made efforts, for removal of trivalent and hexavalent chromium using newly developed functionalized ZnO_2 nanomaterial. The proposed ZnO_2 nanomaterial of varying sizes have been synthesized by wet chemical route using polyvinylpyrrolidone (PVP), triethanolamine (TEA), mercaptopropionic acid (MPA) and Glycerol as capping agent. The details of synthesis process for ZnO_2 nanomaterial using different capping agents is given in our patent [20]. All the functionalized ZnO_2 nanomaterials have been tested for the removal of trivalent and hexavalent chromium, but PVP functionalized ZnO_2 nanomaterial shows excellent adsorption capacity in comparison to other intrinsic and functionalized ZnO_2 nanomaterials. In the proposed study, detailed adsorption studies for trivalent and hexavalent chromium have been done using PVP functionalized ZnO_2 nanomaterial for better removal efficiency.

Materials and Methods

Equipments and apparatus

The synthesis of ZnO_2 nanomaterials of varying sizes were carried out using analytical grade chemicals viz; zinc acetate, ammonium hydroxide, hydrogen peroxide, methanol, PVP, TEA, MPA and Glycerol. All the chemicals were procured from E. Merck India. The trivalent and hexavalent chromium removal studies were carried out in high purity water of 18.2 M Ω-cm resistivity prepared from USA make Millipore milli-Q element water purification system. The trivalent chromium removal studies were done using SCP Science, United Kingdom make certified reference standard solution of 1000

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mg L^{-1} concentration. The same solution was also used for calibration of FAAS after appropriate dilutions. The hexavalent chromium solution of 1000 mg L^{-1} concentration was prepared from high purity potassium dichromate. The left over concentration of total chromium after adsorption was carried out using Analytik Jena make vario-6, FAAS. The pH of the test solutions were optimized using Orion 3-star pH meter procured from Thermo Electron Corporation - United Kingdom. The FTIR spectra of ZnO_2 nanomaterials were measured at room temperature using Perkin Elmer make FTIR Spectrometer. The phase identification of ZnO_2 nanomaterials were done using Bruker Germany make, X-ray diffraction (XRD), model AXS D8 Diffractometer. The morphology of ZnO_2 nanomaterials were done using transmission Electron Microscope, model F-30 G2 STWIN procured from FEI Netherland. The calibrated pipettes and volumetric flasks procured from Borosil Glass Works India Limited were used for dilutions and sample preparation.

Synthesis of ZnO_2 nanoparticles

The intrinsic, MPA, PVP and glycerol functionalized ZnO_2 nanomaterials of varying size were prepared by the reaction of zinc acetate di-hydrate with hydrogen peroxide in ammonical medium (pH 10 ± 1). The desired size of the ZnO_2 nanomaterials were synthesized by varying quantity of capping agent, solvent and temperature of the reaction mixture. The formed precipitates were centrifuged at 10,000-12,000 round minute^{-1} speed as per the sizes of nanomaterials to seprate out from solutions and repeatedly washed with de-ionized water to remove water soluble impurities. Finally purified precipitates were dried at 105°C in an oven.

Characterization

The functionalized ZnO_2 nanomaterials were characterized in 2θ range from 20° to 80° for phase analysis by Bruker make AXS D8 Diffractometer. A representative XRD of PVP functionlized ZnO_2 nanomaterial is given in Figure 1(a). The XRD analysis confirms the formation of single-phase ZnO_2 nanomaterial (PDF # 13-0311) with lattice spacing 0.278 nm for '111' plane. The crystallite size of the ZnO_2 nanomaterial was found to be 9 ± 3 nm using Scherrer's equation, which has been further confirmed by TEM studies (10 ± 3 nm). The broadening of the peaks was estimated by using silicon powder standard reference material procured from NIST USA. The TEM micrograph of ZnO_2 nanomaterial as given in Figure 1(b) shows spherical nature of the nanoparticles. The presence of 'C' and 'Cu' along with 'O' and 'Zn'as given in EDS, insight Figure 1(c) is due to usage of carbon coated copper grid for EDS studies. The EDS analysis also confirms that synthesized PVP functionalized ZnO_2 nanomaterial is free from other ionic impurities.

Determination of point of zero charge

The pH_{pzc} was determined to study the adsorption behavior of ZnO_2 nanoparticles. The pH_{pzc} of a material is that point at which solid surface becomes neutral. It also suggests that below and above of pH_{pzc} the material will be positively and negatively charged respectively. To determine the pH_{pzc} of ZnO_2 nanomaterial three solutions of NaCl of 0.001 M, 0.1 M and 0.5M concentrations were prepared. From each concentration several solutions of 25 mL were taken and pHs were adjusted between 2-11 by 0.01 M HCl and NaOH solution. The pH of each solution was rechecked after 2 hours and then to each solution 5 g L^{-1} ZnO_2 nanomaterial was added. The solutions were stirred slowly on magnetic stirrer and pH was checked after 72 hours. The ΔpH which is equal to difference of initial pH (pH_i) and final pH (pH_f) was plotted against the pH_i for each electrolyte solution. The common point (7.9) of intercept was considered as pH_{pzc} of PVP functionalized ZnO_2 nanomaterial.

Adsorption Study

The adsorption studies were carried out by mixing PVP functionalized ZnO_2 nanomaterial in known amount of trivalent and hexavalent chromium solution. The standard solutions of trivalent and hexavalent chromium were subsequently diluted and pH was adjusted with the help of dilute hydrochloric and sodium hydroxide solutions. Remaining concentration of chromium after adsorption over ZnO_2 nanomaterial was determined by FAAS. The adsorption capacity (q_e) and efficiency were calculated by the following equation (1) and (2):

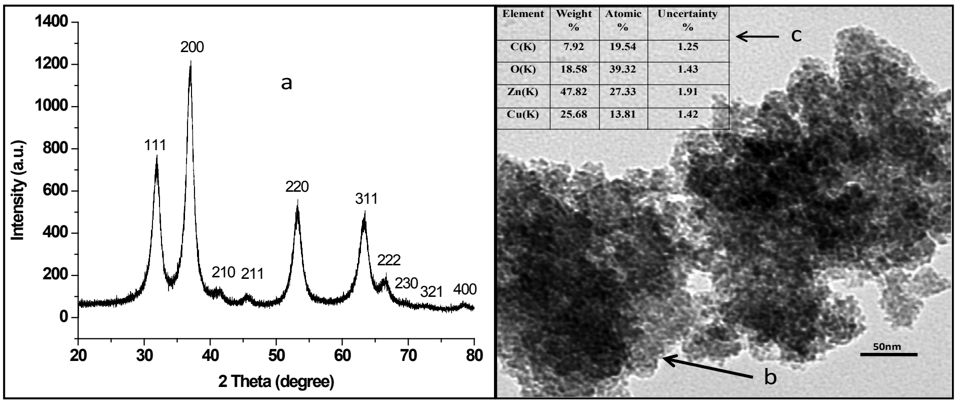
$$Adsorption\ capacity(q_e) = \frac{(c_i - c_f)^* V}{m} \tag{1}$$

$$\%\ removal\ of\ chromium = \frac{(C_i - C_f)^* 100}{C_i} \tag{2}$$

Where, 'C_i' and 'C_f' are the initial and final concentration of trivalent and hexavalent chromium solution (mg L^{-1}), V; volume of solution used (L) and m is the weight of ZnO_2 nanoparticles (g).

The distribution coefficient K_D, which expresses binding ability of chromium on ZnO_2 surface, has been calculated using following equation-3.

$$K_D = C_S/C_W\ (m^3\ Kg^{-1}) \tag{3}$$



Element	Weight %	Atomic %	Uncertainty %
C(K)	7.92	19.54	1.25
O(K)	18.58	39.32	1.43
Zn(K)	47.82	27.33	1.91
Cu(K)	25.68	13.81	1.42

Figure 1: (a) XRD, (b) TEM and (c) EDX (inset) of synthesized ZnO_2 nanomaterial.

Where, C_s is the concentration of adsorbate on the solid particles (mg kg^{-1}) and, C_w is the equilibrium concentration in solution (mg/m^3). The change in K_D value with adsorbent dose at a constant pH has been given in Figure 2. The adsorption data of chromium reveals that the surface of ZnO_2 is heterogeneous in nature.

Result and Discussion

Effect of pH, adsorbent dose, time, and temperature for adsorption

The pH plays a most important role in adsorption process for chromium as it controls the surface charge of the adsorbent and the degree of ionization of the adsorbate in aqueous solution and facilitates the solid and liquid interface during adsorption process. To optimize pH for maximum adsorption several experiment at varying pH (2-11) were carried out in 25 mL solutions containing 50 mg L^{-1} concentration of trivalent and hexavalent chromium. The pH of each test solution was adjusted with the help of 0.001 M solution of HCl and NaOH. In each bottle 250 mg of PVP functionalized ZnO_2 nanomaterial was added, mixed thoroughly, and kept at room temperature for 60 minutes. The decanted solutions were analyzed for remaining concentration of total chromium by FAAS using mixture of air (5 L min^{-1}), acetylene (1.6 L min^{-1}; flame rich) at 357.9 nm wavelength. The effect of pH on removal of chromium has been given in Figure 3(a). From the Figure 3(a) it has been concluded that 6.5-7.3 range is the best range for chromium removal. The removal capacity of proposed ZnO_2 nanomaterial gradually decreases above and below of the optimized pH range.

To optimize adsorption time several experiments were carried out at different time intervals using same amount of adsorbent dose (10 g L^{-1}) and 25 mL volume of 50 mg L^{-1} concentration of Cr (III and VI) solutions. The result for removal of chromium as a function of time is given in Figure 3(b). It has been observed that the removal of trivalent and hexavalent chromium increases on increasing time. The maximum adsorptions were observed in 15 minute. It has been found that 0.14 and 0.18 mg L^{-1} concentration of chromium (III and VI) remains in test solutions after 15 mintes from 50 mg L^{-1} initial concentration of test solutions. On further increasing time no significant changes has been observed, and further all the experiments were carried out at 15 minutes time intervel.

The effect of adsorbents doses were studied (0.5 to 15 g L^{-1}) with 25 mL of 50 mg L^{-1} concentration of trivalent and hexavalent chromium at 15 minute time period at 7.1 pH. The adsorption of chromium increases on increasing adsorbent dose as presented in Figure 3(c). The remaining concentrations of chromium (III and VI) at 8 g L^{-1} adsorbent dose were 0.23 and 0.27 mg L^{-1} respectively, whereas at 10 g L^{-1} adsorbent dose were 0.16 and 0.20 mg L^{-1}. On incresing adsorbent dose to 12 g L^{-1} dose the left over concentration were 0.02 and 0.05 mg L^{-1} respectively. Further on increasing adsorbent dose to 15 g L^{-1}, the remaining concentrations were found below detection limits of FAAS instrument (0.003 µg mL^{-1}) which is much below than the prescribe limit of WHO and EPA (50 mg L^{-1}).

The effects of temperature on trivalent and hexavalent chromium adsorption have also been done at 10-70°C temperature range at optimized pH and time. The lower temperature of the test solutions were done in ice bath, whereas higher temperatures were adjusted by warming test solutions over thermostatic magnetic stirrer hot plate. The maximum adsorption observed between temperatures 23-38°C, whereas adsorption gradually decreases on increasing or decreasing temperature of the test solutions. The effect of temperature on chromium adsorption has been given in Figure 3(d).

Isotherm model

Adsorption isotherm studies have been carried out at varying concentrations of chromium from 5 to 50 mg L^{-1} in pH range 6.5 to 7.3 All the experiments were carried out in 25 mL solutions of 50 mg L^{-1} concentration of Cr (III and VI) using 0.25 g adsorbent dose. It has been found that 0.14 and 0.18 mg L^{-1} of chromium (III and VI) remains in the test solutions from 50 mg L^{-1}, 0.07, and 0.08 mg L^{-1} from 30 mg L^{-1} and 0.01 mg L^{-1} from 25 mg L^{-1} concentration. However remaining concentrations of Cr (III and VI) were below detection limit of FAAS, when concentrations were less than 20 mg L^{-1}. The percent removal of chromium on decreasing concentration has been given in Figure 4. The details of results are given elsewhere [21].

The adsorption data were fitted to Freundlich, Langmuir and Dubinin Raduskevich isotherm to find out reaction mechanism. The Freundlich isotherm denotes heterogeneous behavior of the adsorbent and can be quantify using following equation-4.

$$\ln(\frac{x}{m}) = \ln k + \frac{1}{n}\ln C \quad (4)$$

Where 'k' is the Freundlich constant, '1/n' is the adsorption intensity, 'C' is the equilibrium concentration (mg dm^{-3}) and 'x m^{-1}' is

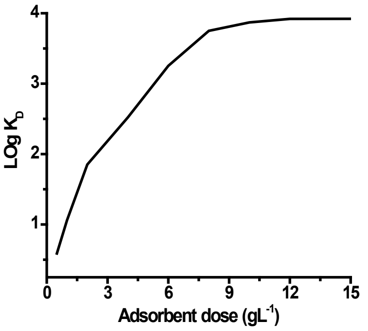


Figure 2: Plot of adsorbent dose (g L^{-1}) vs. Log K_D.

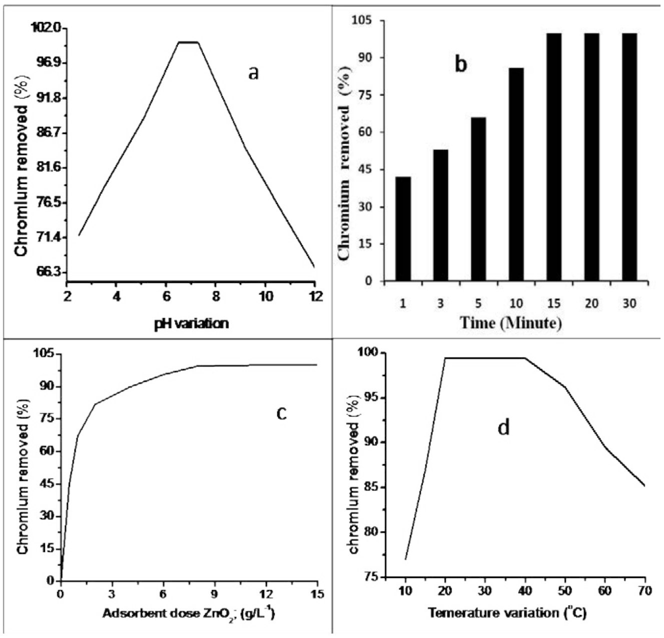


Figure 3: Effect of (a) pH, (b) time, (c) dose and (d) temperature on adsorption.

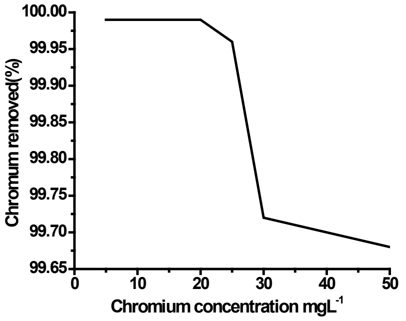


Figure 4: Isotherm plot for Chromium removal on varying concentration.

the amount adsorbed at equilibrium (mg g^{-1}). The values of 'k' and '1/n' can be calculated from the slope and intercept of the linear plot of 'ln q' against 'ln C'. The calculated data for 'k', '1/n', and 'R^2' were found to be 0.232, 1.748 and 0.118, respectively.

The Langmuir isotherm denotes monolayer adsorption over adsorbent surface and can be represented in equation form as follows;

$$\frac{C}{x/m} = \frac{C}{Q} + \frac{1}{bQ} \tag{5}$$

Where 'C' is the equilibrium concentration (mg dm^{-3}); 'xm^{-1}' is the amount adsorbed at equilibrium (mg g^{-1}) and 'Q' and 'b' are the Langmuir constants related to the capacity and energy of adsorption respectively. The Langmuir constants 'Q' and 'b' can be calculated from slope and intercept of linear regression plot between 'C/x/m' and 'C'. The calculated value of 'Q', 'b', and 'R^2' were found to be 0.004, -0.013, and 0.472, respectively.

In the same way the equilibrium data was fitted to the Dubinin Raduskevich isotherm model. The free energy of sorption can be determined using logarithmic linearized equation as given below:

$$\ln X = \ln X_m - K\varepsilon^2 \tag{6}$$

Where 'ε'(polanyi potentiali)= RT ln(1+(1/C)), 'ln X' is the amount of adsorbate adsorbed per unit weight of adsorbent (g g^{-1}), 'ln X_m' is the adsorption capacity (g g^{-1}) of the adsorbent, 'C' is the equilibrium concentration of adsorbate in aqueous solution (g L^{-1}), 'R' is the gas constant and 'T' is the temperature in Kelvin. The 'K' is the adsorption energy constant, The 'K' and 'X_m' values can be derived from the slope, and intercepts value of the plot of 'ln X' against 'ε^2'. The free energy of adsorption 'E' can be calculated from the 'K' value using equation-7.

$$E = (-2K)^{-0.5} \tag{7}$$

The value of 'K' (mol^2/kJ^2), 'Xm' (mol/g) and 'R^2'were found to be 0.479, 6.245 and 0.977, respectively. The value of 'E' using equation - 7 was found to be 1.022. On comparison of all the three adsorption isotherms utilized the adsorption data was perfectly fitted with Dubinin Raduskevich isotherm model having 'R^2' value greater than 0.977. The sorption behavior observed for chromium using ZnO_2 nanomaterial was purely physical adsorption.

Effect of foreign ions on chromium adsorption

The adsorption capacity of ZnO_2 nanomaterial has also been carried out in tap water, to check the real efficiency of nanomaterial in presence of several ions like nitrate, sulphate, chloride, phosphate, calcium, magnesium, sodium, iron, calcium usually present in underground water. The TDS and pH of tap water was 650 mg L^{-1} and 7.1, respectively. The concentration of sodium and calcium was around 1500 mg L^{-1}, whereas concentration of other above mentioned ions were from 5-40 mg L^{-1}. The dilutions of trivalent and hexavalent chromium standard stock solution upto 20 mg L^{-1} were done directly in tap water and to each solution 0.25 g of ZnO_2 was added and kept at room temperature for 15 minutes. The decanted tap water was tested for remaining concentration of chromium by FAAS at optimized conditions. In this case it has been observed that Chromium can be removed without any interference of common ions of tap water.

Leaching studies

The chromium leaching studies from ZnO_2 nanomaterial were carried in fresh water. The leaching studies of chromium were carried out using the adsorbed ZnO_2 for regeneration at different pH. For chromium leaching experiments several sets of 0.25 g of utilized ZnO_2 were added in 25 mL of fresh water (6.8-7.2) and stirred slowly for 1 hour. The decanted water was tested for leached out chromium. It has been observed that leached out chromium concentration was below detection limit of FAAS. Further same experiments were repeated at different pH using 0.001 N HCl and 0.001 N NaOH solutions. It has been observed that in lower pH, in presence of hydrochloric acid some ZnO_2 gets dissolve and chromium releases in water probably as $CrCl_3$. In the same way in higher pH, leaching of chromium starts at the pH ranges of 8.9-9.2 and completed at pH about 11.9 in all the cases.

TEM studies

The TEM along with EDX studies were carried out after depositing test material over carbon coated copper grid of 200 mesh size. The TEM of ZnO_2 nanomaterial along with EDX data has been given in Figure 5. The ZnO_2 nanoparticles as given in Figure 1(b) show the spherical nature of synthesize material and boundry of the individual particles are distinct. The ZnO_2 particles get dispersed in test water, but after chromium adsorption agglomeration takes place and ZnO_2 nanoparticles settled down in the bottom within 15-20 minutes. The EDX of ZnO_2 nanoparticles as given in Figure 5 confirms the adsorption of chromium over ZnO_2 surfaces, while presence of 'C' and 'Cu' along with 'Zn' and 'Cr'is due to usage of carbon coated copper grid for TEM and EDS studies.

FTIR studies

FTIR studies of ZnO_2 nanoprticles have been carried out before after trivalent and hexavalent chromium removal process. FTIR spectra of pure ZnO_2 and after chromium adsorption were measured at room temperature by mixing nanomaterial with KBr. The FTIR spectra of pure, traivalent and hexavalent chromium has been given in Figure 6. In the adsorption process the ZnO_2 nanomaterial adsorb chromium from contaminated water over the surface or probably forms zinc chromate ($ZnCrO_4$). This species is insoluble in water, agglomerates and get settled down in the water. The TEM micrograph as given in Figure 6 confirms the adsorption of these species over the surface of ZnO_2 nanomaterial. The absorption peaks in the 3200–3600 cm^{-1} range is due to O–H stretching vibration mode, while bands at 1630–1660 cm^{-1} range is due to -OH bending of water. It also exhibits presence of water molecules adsorbed over ZnO_2 nanoparticles. The peak around 2360 cm^{-1} shows existence of CO_2 molecule in the ambient air. The absorptions at 435–445 cm^{-1} and 1040–1070 cm^{-1} are due to ZnO_2 [22]. A large band appears in the range 450-700 cm^{-1} and at ~940 cm^{-1} can be assigned to Cr–O bond vibrations [23].

The adsorption efficiency of ZnO_2 nanomaterial increases as the particles sizes reduces. On decreasing particles size surface area of the material increases and less amount of ZnO_2 nanomaterial is sufficient to remove chromium than bigger size ZnO_2 particles. We have synthesized ZnO_2 nanomaterial of 5-50 nm ranges functionalized with PVP, TEA, MPA, and glycerol. In preliminary studies we have tested intrinsic and functionalized ZnO_2 nanomaterials. But PVP functionalized ZnO_2 nanomaterial was found more effective in comparison to TEA, MPA and glycerol functionalized ZnO_2 nanomaterial. The particles of bigger sizes after chromium adsorption gets settled down within 15-20 minutes and can be separated easily from water. But the ZnO_2 nanoparticles less than 10 nm size float in the water and takes hours for settling or required centrifuge process. It is observed that at higher pH, the adsorption capacity of ZnO_2 decreases drastically, probably due to formation of complexes with excess hydroxide ions. In the same way adsorption capacity of ZnO_2 decreases drastically due to solubility of nanomaterial in lower pH.

Most of the experiments were carried out in freshly prepared de-ionized water. After several experiments it has been concluded that ZnO_2 does not alters pH of water. The pH of water was checked before addition of ZnO_2 nanoparticles and after removal of chromium and it has been found that there were no significant changes in the pH of the water. During the adsorption process no buffer solution has been used to adjust the pH. Besides this, the left over concentration of zinc and acetate ions in the filtrate water has been analyzed by Atomic Absorption Spectrometer and Ion Chromatograph respectively. In all the cases concentration of zinc and acetate ions were always found below detection limits of AAS and Ion chromatograph. The main reason is that the synthesized ZnO_2 were repeatedly washed several times with solvents like alcohol and de-ionized water.

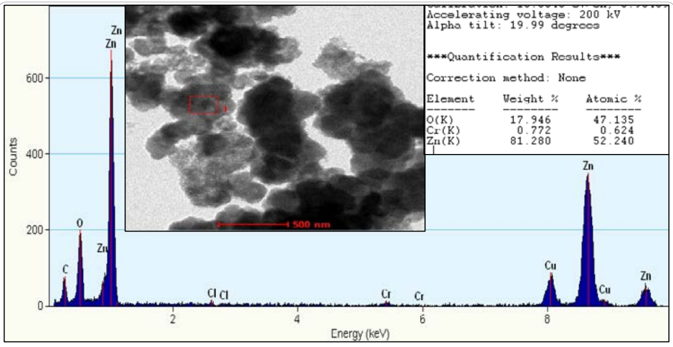
The adsoption capacity of ZnO_2 nanomaterial has been compared with some other adsorbents cited in the literature.The detilas of pH, time and temperature for functioning of different adsorbent has been given in in table-1. The tables reveals that the proposed nanomaterial efficiently works in the range of 6.5-7.3 pH ranges, which is common ranges of the contaminated water. So there is no requirement of any acid or base for adjustment of pH for funtioning of ZnO_2 nanomaterial. It has been concluded from the table that proposed material have several advantages in terms of time, adsorptioncapacity in comparison to other materials cited in the literature [24-27].

Data accuracy

To ensure the qulatity of data, we have used certified reference material for determination of chromium at optimized conditions of pH, time, adsorbent dose, etc. The calibration of FAAS instrument for chromium determination was carried out using certified reference material after subsequent dilutions by gravimetrically upto the range of analyte sample. All the analysis was carried out three times to get repeatable results and average of three values have been used for final calcultions. The weighing of ZnO_2 materials were carried out using Mettler Toledo makes balance. The balance was calibrated by CSIR-NPLI following international protocols and procedures. In the same way all the apparatus like volumetric flask, pippets, thermometer etc were get calibrated from CSIR-NPLI prior to use. A process blank has also been prepared and analyzed in the same way and correction applied in final calculations.

Conclusion

A novel application of PVP functionalized ZnO_2 nanomaterial has been presented as a potential nanomaterial for the removal of triavalent and hexavalent chromium from contaminated water. The ZnO_2 nanomaterial is insoluble in water and soluble particles if any separate out during purification process. To confirm, left over concentration of zinc and acetate ions in the filtrate water were analyzed by Atomic Absorption Spectrometer and Ion Chromatograph respectively and concentration of these ions were always found below detection limits of AAS and IC system. The proposed nanomaterial due to high surface area effectively adsorb chromium and make it suitable for human consumption. The SEM-EDX and FTIR also confirm adsorption of chromium on the surfce of ZnO_2 nanomaterial. The Kinetic study reveals that proposed nanomaterial effectively removes more than 99.9% of chromium within 15 minutes. The adsorption studies data were best fitted with Dubinin Raduskevich isotherm model and suggests purely physical adsorption over surface of ZnO_2 nanoparticles. During the adsorption process, the pH of water does not alter and there is no need to adjust the pH using acid or alkali. So purify water can be safely used for several application in house including drinking. The PVP is also biocompatible and there is no side effect of the material. The proposed material can be used in remote areas and also suitable for low income people.



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Accelerating voltage: 200 kV
Alpha tilt: 19.99 degrees

***Quantification Results***

Correction method: None

Element     Weight %     Atomic %
-------     --------     --------
O(K)          17.946       47.135
Cr(K)          0.772        0.624
Zn(K)         81.280       52.240
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Figure 5: TEM and EDX of ZnO_2 powder after chromium removal.

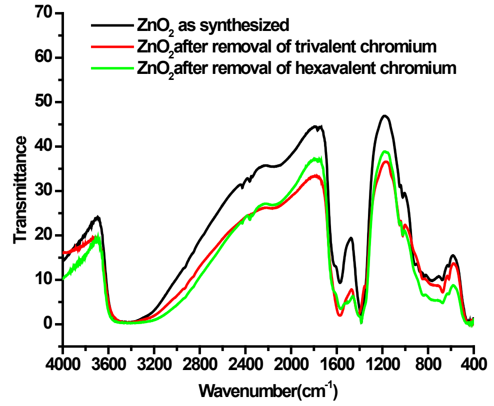

Figure 6: FTIR of ZnO_2 before and after removal of trivalent and hexavalent chromium.

S.N.	Name of adsorbent	Adsorption capacity (mg/g)	Time	pH	Ref.
1.	Silica	1.5	-	2-4	24
2.	HDTMA-Modified Zeolites Cowlesite	0.763	-	7	25
3.	Clinoptilolite HDTMA	0.844	-	7	26
4.	Red clay	1.3	-	4 - 6.5	27
5.	ZnO_2 nanomaterial	4.98	15	6.5-7.3	Present study

Table 1: Adsorption comparision of PVP functionalized ZnO_2 nanomaterial for chromium.

The following outcomes have been observed in the present investigation:

1. Dubinin - Raduskevich isotherm model fitted well to the present study and physical adsorption plays an important role in adsorption process.
2. TEM and EDS studies reveals physical adsorption of chromium over ZnO_2 nanoparticles, which has been further confirms from the D-R isotherm model.
3. The PVP functionalized ZnO_2 nanomaterial safely remove 20 mg L^{-1} of chromium (III&VI) below detection limit of FAAS. Whereas 0.07 and 0.08 mg L^{-1} of chromium (III and VI) remains from 30 mg L^{-1} and 0.14 and 0.18 mg L^{-1} from 50 mg L^{-1}.

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