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Iron Functionalized Zinc Peroxide nanomaterial for removal of Arsenic and Chromium from contaminated water

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ABSTRACT

In the present research work we have done some preliminary work related to water purification especially contaminated by arsenic and chromium. We have synthesized iron functionalized ZnO_2 nanomaterials of varying sizes characterized the phase of iron functionalized ZnO_2 nanomaterial by XRD, shape and particle size by SEM, TEM and particle size by Microtech particle analyser. It was further characterized by Dynamic Light Scattering (DLS) method in order to determine their average particle size and magnitude of the overall charge on the nanoparticles and have been used for expatriation of arsenic and chromium. The proposed nanomaterials are of low cost, non toxic and highly efficient in removing arsenic and chromium from drinking water. The proposed nanomaterials purify arsenic and chromium contaminated water up to the permissible range of drinking water. The arsenic and chromium removal efficiency of iron functionalized ZnO_2 nanomaterial are taken at different time interval and pH range. It has been concluded from the observation that iron functionalized ZnO_2 nanomaterial is more effective and removes arsenic and chromium, below detection limit of FAAS/ AAS-HG (Atomic absorption spectroscopy (AAS)). The purified water can be used for drinking purpose and other house hold utilities. We have made attempt for the appropriate removal of heavy metals (Arsenic and Chromium) from contaminated water below the prescribed limit of World Health Organization (WHO) and Environmental Protection Agency (EPA) by using low cost, iron functionalised zinc peroxide nanomaterial.

KEY WORDS: ZnO_2 nanomaterial, Iron functionalized ZnO_2 nanomaterial, Arsenic and Chromium removal, Environmental Protection Agency, World Health Organization.

1. INTRODUCTION

Worldwide several countries mainly developing country are suffering from water borne diseases because of the toxic contaminations in water, discharge from industries and transport sector. The demand of pure water is increasing because most of the water reservoirs are getting contamination and water level is going very down. It is the direct effect of population growth and extended drought (Quick, 1997). Over the past 20 years, about 1.5 billion people are suffering from contamination of drinking water. The quality of drinking water can affect by natural and anthropogenic activities (Yu, 2004). These activities can produces many types of contaminates like organic, inorganic (heavy metals), and biological. This is one of the major reasons of death all over the world. Heavy metals pollution is becoming one of the most serious environment problems globally (Fujita, 2014; Al-Musharsfi, 2013; Naser, 2013; Akinci, 2013). It is still the challenging task to remove the undesirable metals from the water system. It can causes the dangerous health problems including the reduced growth and development, cancer, organ damage, nervous system damage and in utmost cases death. Many metals are highly toxic and carcinogenic in nature. Even if they are present at low concentration in water, can pose a significant threat to human and ecosystem health. To protect water sources, wastes must be properly treated before they are discharge to watercourses (Chambers, 2000; Environment Canada, 2001). WHO (World Health Organisation) (Environment Canada, 2009) or EPA (Environmental Protection Agency) have proposed a guideline for the maximum allowable limits in water, like total pesticides should not be more than 0.3ppm, arsenic <10ppb, chromium <50ppb, nitrites 50ppm. Toxicological studies (Babel, 2003) have shown that the Heavy metal ions toxicity depends on its oxidation state. For example Chromium present in industrial effluents is usually introduced in the environment in two stable oxidation states +3 and +4, Cr (III) is a vital micro nutrient for plants and animals whereas Cr (VI) is soluble and hazardous to health. In natural water chromium ions generally appear as chromate and cationic hydroxo complexes. The recommended limits of chromium (VI) in potable water is 0.05 ppm (Hall, 2002). Arsenic exists in two forms Inorganic and organic. Inorganic Arsenic is carcinogenic in nature. Maximum acceptable concentration (WHO) for arsenic is 0.01mg/l or 10 ppb. Heavy metals toxicities is all because of its interaction with certain ligands of amino acids, inhibition and reduction of various enzymes in the body and substitution of vital metal ions from enzymes.

There are so many techniques and adsorbent materials that are being used for removal of heavy metals from contaminated water like photo catalytical oxidation, chemical coagulants, electrochemical, bioremediation, ionexchange resins, reverse osmosis, and adsorption (Fu, 2011; Hashim, 2011). But most of the techniques have many drawbacks, such as high maintenance & costs for treatment (Murray, 2001). Thus we have synthesized cheap and cost effective nanomaterials that can be used for the removal of heavy metals (As and Cr) from contaminated water. Conventional techniques are available for the removal of heavy metals from the liquid phase. These techniques mainly are solvent extraction, evaporation and coagulation and so on. Treatment of heavy metal by conventional technique has limitations such as (i) its required high skilled operator (ii) demands higher energy requirement because sometime microflocs formed which is often difficult to remove.(iii) the process is expensive for treatment of toxic sludge and other waste product not more achievable with high levels of TDS (Payment, 1991). Therefore these technologies are expensive in investment cost, high cost and complex for removal of arsenic and chromium from contaminated water. Keeping above facts an attempt has been made for the appropriate removal of heavy metals (As and Cr) from contaminated water below the prescribed limit of World health organization (WHO) and Environmental Protection Agency (EPA) by using low cost, iron functionalised zinc peroxide nanomaterial. Application of iron oxide based nanomaterial is now considered as one of the best technique for removal of heavy metals contamination from the water because of its unique characteristics property like low toxicity, chemical inertness, biocompatibility and super para magnetism (Xu, 2012; Warner, 2012; Karatapanis, 2012; Yang, 2012). It is environmentally friendly. Today research is going on use of nanotechnology for water purification because of their intense response due to their wide surface area and volume ratio (Hua, 2012; Kharisov, 2012; Feng, 2012).

2. EXPERIMENTAL

Materials/ Chemicals details: All the chemicals used for the synthesis of intrinsic ZnO_2, iron functionalised ZnO_2 and determination of arsenic and chromium by AAS like sodium borohydride ($NaBH_4$), ethanol (C_2H_5OH), zinc nitrate ($ZnNO_3$), zinc sulphate ($ZnSO_4$), zinc chloride ($ZnCl_2$), Ferrous Sulphate ($FeSO_4$), hydrogen peroxide (H_2O_2), polyvinyl pyrrolodone (PVP), zinc acetate ($Zn\ (CH_3COOH)_2$), methanol (CH_3OH), ammonium hydroxide (NH_4OH), 3-Mercaptopropanoic, acetone etc. used were of analytical grade (E. Merck). 35% of HCl of GI grade was also used. All the solutions were prepared in de-ionized water. The reference standards stock solution of 1.0 mg/litre (BND 301.03; NPL-India) of arsenic and 1000 mg/litre of chromium solution of SCP make were used for calibration of AAS instrument after subsequent dilutions. For arsenic removal studies 1000 mg/litre of Merck-Germany make standard reference solution, arsenic acid (H_3AsO_4) solution prepared after dissolving arsenic oxide (As_2O_3) in nitric acid have been used. While for chromium studies 1000 mg/litre of SCP Science standard reference solution and chromium (VI) standard solution prepared after dissolving high purity potassium dichromate in de-ionized water. All these solutions were used after subsequent dilutions. All the acid dissolution, dilutions work was carried out in laminar flow bench with ventilation systems. The weighing work has been done using Ohaus make, GD 200 model balance. An oven (SE Heatech Silgomelt Pizautovens), a hot plate (Ambassador), Centrifuge (Remi C-24 plus) ultra-sonicator (Elma transonic T 700-H), and magnetic stirrer (Remi equipment Pvt. Ltd.) have been used to dry the precipitate at 120^0C and to digest the test sample respectively.

The synthesized intrinsic and iron functionalised ZnO_2 powders were characterized by XRD (X-Ray diffraction) using Bruker AXS D8 advance diffractometer. Diffractograms were recorded using CuKα radiation with a graphite monochromator in the diffracted beam. The structural analysis of synthesized materials before and after arsenic and chromium removal were examined by using Scanning electron microscope, FEI make transmission Electron Microscopy (TEM), Netherland, F-30 G2 STWIN, FEG operated at 300 kV. Analytic Jena make, vario-6 model Atomic Absorption Spectrometer-Hydride Generator (AAS-HG) has been used for determination of arsenic and total chromium. Particle size of as synthesized iron oxide doped zinc peroxide nanostructure was measured by Malvern particle size analyzer (Model Micro-P, range 0.05-550 micron).

Material synthesis:

Synthesis of intrinsic zinc peroxide: Intrinsic zinc peroxide was prepared by 10g of zinc acetate and 2g Polyvinyl Pyrrolodone (PVP) were poured into a 1 litre beaker containing 400ml of methanol in it with constant stirring using kabin scientific instrument at temp $50^0\pm2^0$C. During stirring added small amount of dilute solution of ammonium hydroxide (1:4 water: ammonia) of NH_4OH in the resulting solution. White precipitate was formed then NH_4OH added again up to completely dissolution of precipitate. To this solution added 30ml of 30% H_2O_2 drop by drop with constant stirring and stirred for half an hour. After that solution had been cooled at room temp and centrifuged 7000-8000rpm, repeatedly was washed with boiled de-ionized water followed by 2-3 times washing with solvent to make sure complete removal of free hydrogen peroxide and water/ solvent soluble material. Finally the precipitate was dried 105^0C for 6-7 hours. The precipitate was grind in a pestle motor (Singh, 2015).

Synthesis of iron functionalized zinc peroxide (Set-1):

Preparation of zinc solution (Sol A): Zinc solution was prepared by 20g of zinc acetate and 12g of PVP were poured into a 1 litre beaker containing 100ml of distilled water and steadily added 300ml methanol in it and it was appeared as complete dissolved transparent solution. And then added drop by drop 1:1 ammonia solution in the reaction mixture kept at 50^0C with constant stirring. At the starting the salt completely dissolved in reaction mixture with little bit turbidity which disappeared on adding again ammonia solution as per requirement.

Preparation of iron solution (Sol B): Iron solution was prepared by 4g of $FeSO_4$ and 3g of PVP poured into a beaker containing 150 ml of 1:1 methanol and distilled water.

Preparation of ferric doped zinc peroxide: In solution A, 2.5ml of MPA (mercapto propanoic acid) was added and stirrer for 20 min and then added Solution B in Sol A drop after drop while constantly stirring using kabin scientific instrument at temp $55^0 \pm 5^0$C. As time went, the resulting solution becomes greenish yellow color. To this solution equimolar quantity of 1:1 H_2O_2 diluted was added drop by drop. White precipitate forms and it was stirred for 1 hour. After that solution had been cooled at room temp and precipitate was centrifuged at 7000-8000 rpm and repeatedly was washed with boiled de-ionized water followed by 2-3 times washing with solvent to make sure complete removal of free hydrogen peroxide and water / solvent soluble material. Finally the precipitate was dried 105^0C for 6-7 hours and was grind in a pestle motor.

Synthesis of ferric functionalized zinc peroxide (Set-2):

Preparation of zinc solution (Sol A): Zinc solution was prepared by 20g of zinc acetate and 20g of PVP were poured into a beaker containing 150ml of distilled water and gradually added methanol until it was appeared as complete dissolved transparent solution. And then added drop by drop 1:1 ammonia solution in the reaction mixture was kept at 50^0C with constant stirring. At the starting the transparent solution gives white precipitate of zinc hydroxide and then added excess of 1:1 ammonia until get the complete dissolution of precipitate in the reaction mixture.

Preparation of iron solution (Sol B): Iron solution was prepared by 6g of $FeSO_4$ and 8g of PVP poured into a beaker containing 100 ml of 1:1 methanol and distilled water.

Preparation of ferric doped zinc peroxide: In solution A, added Solution B drop by drop with constant stirring using Kabin scientific instrument at temp $55^0 \pm 5^0$C. As time went, the resulting solution becomes yellowish brown colour. To this solution equal molar of 1:1 H_2O_2 diluted was added drop by drop and then the solution turned to dark brown from yellowish brown colour. After that solution had been cooled at room temp and precipitate was centrifuged at 7000-8000 rpm and repeatedly was washed with boiled de-ionized water followed by 2-3 times washing with solvent to make sure complete removal of free hydrogen peroxide and water / solvent soluble material and divided into two parts. One half part of centrifuged dried at 105^0 C for 6-7 hours and grind in a pestle motor other half part added 2g sodium oleate and 100ml distilled water. The synthesized intrinsic zinc peroxide and iron functionalized zinc peroxide nanomaterial powders were characterized for various phases by X-ray diffraction (XRD). The morphology of synthesized materials before and after arsenic and chromium removal was examined by using Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM). Scanning electron microscope (SEM) has been used for examine the surface morphology of the sample and transmission electron microscope (TEM) has been used to investigate the microstructure of synthesized iron oxide powder

Experimental Work of AAS (Atomic Absorption Spectrometer):

AAS (atomic absorption spectrometer): Hydride Generator was used in AAS to determine arsenic at wavelength 193.7nm, 0.2nm (slit) and argon (100ml/min) as a carrier gas, after reducing arsenic (V) in Arsenic (III) by potassium iodide and ascorbic acid. The volatile AsH_3 is formed by the reaction between sodium borohydride 3% as a reducing agent and HCl 5% with arsenic which atomize at 900 °C. While the determination of chromium has been done up to ppm level by FAAS using mixture of air (5litre/minute) and acetylene (1.5litre/minute flame rich) at 357nm wavelength and 0.5 nm slit. The lower concentrations were determined by GFAAS using argon as carrier gas Arsenic and chromium, removal studies were carried out using AAS-HG and FAAS respectively. The calibration of AAS-HG and FAAS was done using different calibration standards.

Effect of pH on removal of Arsenic and Chromium: The pH plays a vital role in adsorption process for arsenic and chromium as it regulates the adsorbent' s surface charge and the degree of ionization of the adsorbate in aqueous solution and it also eases the solid and liquid interface during adsorption process. For arsenic removal studies a stock solution of 10.038ppb was used after subsequent dilutions, where as for chromium 1000ppm standard stock solution was used after appropriate dilutions. The stock solution was diluted up to 1ppm range. Two sets (Six each) of iron functionalised ZnO_2 for arsenic & chromium of different pH were taken in separate pre-clean and dried beakers. The pH of each set was measured using calibrated pH meter. To optimize pH for maximum adsorption several experiment were carried out by adjusting the pH of the solutions around; 3.5, 4.8, 6, 7.5, 8.5, and 10 using 0.001M hydrochloric acid (HCl) and 0.001M Ammonium hydroxide (NaOH). In each bottle 100mg of synthesized intrinsic and iron functionalised ZnO_2 were added to each solution. The solutions were ultra-sonicated and were kept at room temperature for 60 minutes. The solutions were then tested for the left over concentration of arsenic, and chromium using AAS-HG (atomic absorption spectrometer –hydride generator) for determination of arsenic zeenit-60, Analytik Jena make, Graphite Furnace Atomic Absorption Spectrometer (GFAAS) was used for determination of low concentration of chromium using argon as carrier gas.

Effect of Time on Arsenic and Chromium Adsorption: Experiments were carried out at different time intervals in order to optimize adsorption time. Time intervals set was 5, 10, 20, 30, 35 and 40 minutes using same amount of adsorbent dose of Chromium and arsenic solutions.

3. RESULT AND DISCUSSION

XRD: The intrinsic ZnO_2 were recorded in diffraction patterns 2θ range from 20^0 to 80^0. All diffractions peaks were correspond to ZnO_2 conforming formation of single phase material in each case. Scherer's equation was used to estimate the crystallite sizes of zinc peroxide. A representative XRD of ZnO_2 (fig.1a). XRD of synthesized intrinsic zinc peroxides nanomaterial shows pure phase of zinc peroxide and HRTEM micrograph shows spherical nature of the nanoparticles and figure.1b shows the TEM image of synthesized intrinsic ZnO_2. Figure 2a shows that pure phase of ferric hydroxides and zinc peroxide iron functionalised zinc peroxide nanoparticles. The synthesized materials are in nano meter range and it is crystalline in nature was confirmed by the sharpness of peak

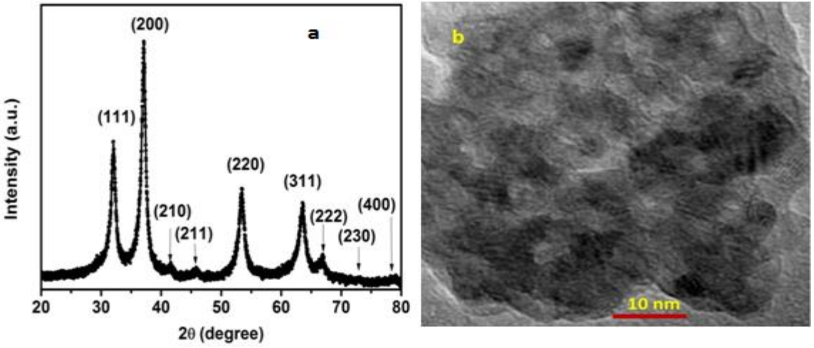

Figure.1a. XRD of intrinsic ZnO_2 and figure.1b. TEM image of intrinsic ZnO_2

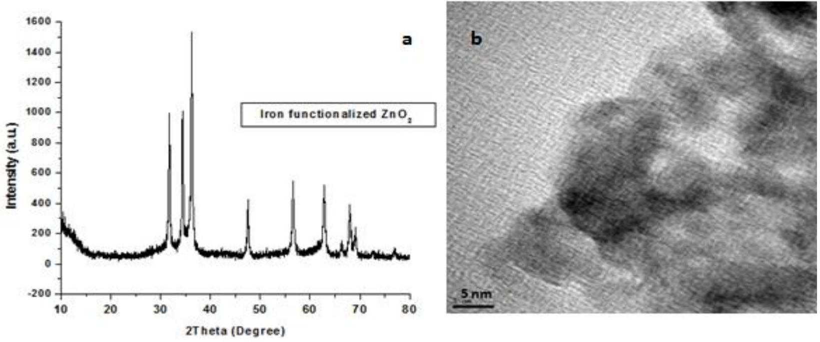

Figure.2a. XRD of iron functionalised ZnO_2 and figure.2b. TEM image of iron functionalised ZnO_2

TEM: Figure 1b represents the TEM micrograph of ZnO_2 as synthesized with lattice spacing of about 0.278 nm (~ 2.8 Å for the (111) plane in the cubic ZnO_2. The micrograph shows that the product is composed of micro spheres with diameters of 15-20 nm. There is a clear agglomeration in the sample but all the spheres have a distinct boundary. Using Scherrer's equation, the ZnO_2 nanomaterial's crystallite size was found to be 9 ± 3 nm, which was further proven by TEM studies (10 ± 3 nm).

Particle Size Distribution: The average size of iron functionalized ZnO_2 nanoparticles was found to be 143.7 nm.

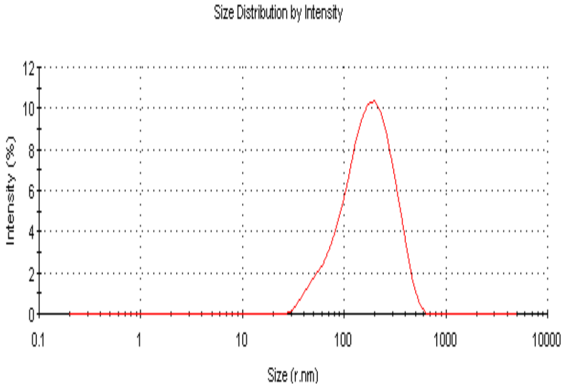

Figure.3. The particle size distribution of chemically synthesized iron functionalized ZnO_2

Table.1. Particle size Distribution by Intensity of iron functionalized ZnO_2

Sample	Z-Average	PDI	Peak	size (r.nm)	Width (r.nm)	Intensity%
Iron functionalized ZnO_2	143.7	0.232	1	191.3	101.10	100

Effect of pH on Arsenic Adsorption:

Table.2. Effect of pH on arsenic adsorption using Fe, Functionalized ZnO_2

Material used	pH variation	Arsenic taken (ppb)	Arsenic removal (ppb)
Iron functionalised ZnO_2	3.7	1000	825
	4.9	1000	887
	6.6	1000	999
	7.6	1000	998
	8.4	1000	885
	9.9	1000	745

From the table.2, it has been concluded that at pH range 6.6 to 7.6, maximum absorption take place in 40 min. So, next experiment has been done for maximization of time at same concentration (1000ppb).

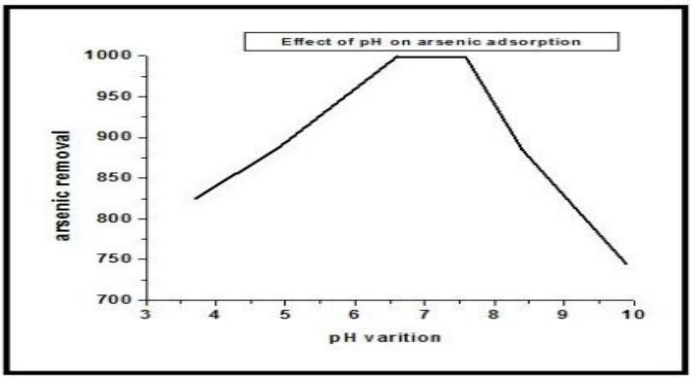

Figure.4. Effect of pH on arsenic adsorption using Fe, functionalized

The effect of pH on removal of Arsenic is given in figure 4 and it has been concluded that 6.6-7.6 range is the best range for chromium removal. The removal efficiency of Iron functionalized ZnO_2 nanomaterial sequentially decreases above and below of the optimized pH range.

Effect of Time on Arsenic Adsorption:

Table.3. Effect of time on arsenic adsorption using Fe, functionalized ZnO_2 at 6.5-7.5 pH range

Material used	At constant pH	Time (in min)	Initial conc. of arsenic (ppb)	Arsenic removal (ppb)
Iron functionalised ZnO_2	6.5-7.5	5	1000	598
	6.5-7.5	10	1000	765
	6.5-7.5	15	1000	840
	6.5-7.5	20	1000	919
	6.5-7.5	25	1000	955
	6.5-7.5	30	1000	998
	6.5-7.5	35	1000	999
	6.5-7.5	40	1000	998

From table.3, it is evident that maximum absorption occurs within 30min at pH 6.5-7.5. On further increasing time no significant changes has been observed.

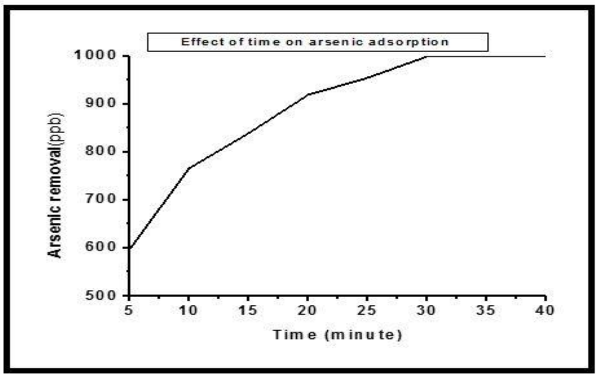

Figure.5. Effect of time on arsenic adsorption using Fe, functionalized ZnO_2 at 6.5-7.5 pH range

Effect of pH on Chromium Adsorption:

Table.4. Effect of pH on Chromium adsorption using Iron functionalised ZnO_2

Material used	pH variation	Chromium taken (ppb)	Chromium removal (ppb)
Iron functionalised ZnO_2	3.4	1000	832
	4.7	1000	863
	6.1	1000	986
	7.5	1000	988
	8.3	1000	854
	9.5	1000	750

From the table.4, it has been concluded that at pH range 6.1 to 7.5, maximum absorption take place in 40 min. So, next experiment has been done for maximization of time at same concentration (1000ppb).

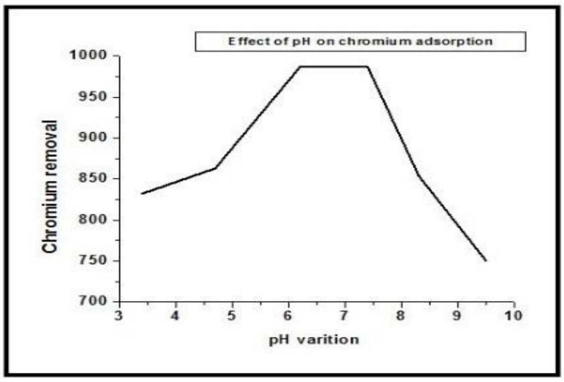

Figure.6. Effect of pH on Chromium adsorption using Fe, functionalized ZnO_2

Table.5. Effect of time on Chromium adsorption using Fe, functionalized ZnO2 at 6.1-7.5 pH range

Material used	Time (in min)	Initial conc. of chromium (ppb)	Chromium removal (ppb)
Iron functionalised ZnO_2	5	1000	645
	10	1000	777
	15	1000	858
	20	1000	939
	25	1000	965
	30	1000	993
	35	1000	993
	40	1000	995

From table.5, it is evident that maximum absorption occurs within 30min at pH 6.1-7.5. On further increasing time no significant changes has been observed.

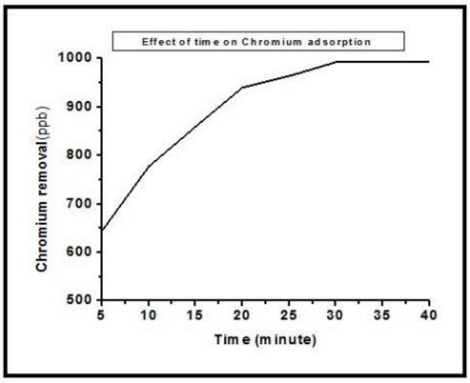

Figure.7. Effect of time on Chromium adsorption using Fe, functionalized ZnO_2 at 6.1-7.5 pH range

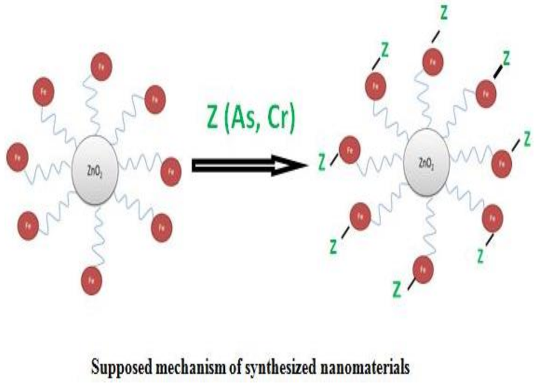

Figure.8. Graphical Abstract

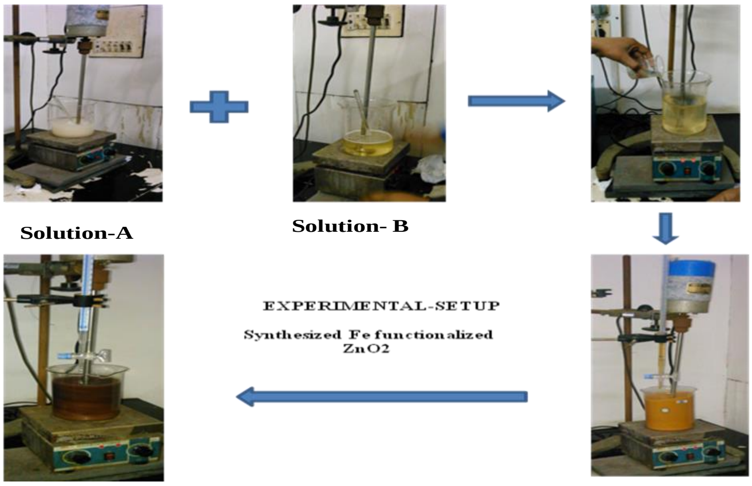

Figure.9. Experimental setups/ Schematics for Preparation of synthesized iron functionalized ZnO_2

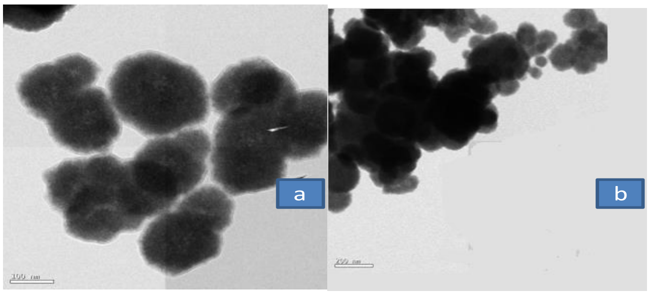

Figure.10. Iron functionalised ZnO_2 after removal of arsenic (a) and chromium(b)

4. CONCLUSION

The Iron functionalized ZnO_2 are good adsorbent and insoluble in water. Therefore it increases the reactivity of zinc peroxide by adding in it. The pH of water does not change after treatment with nanoparticles. This is a facile method of preparation and eco-friendly .The recovery is more than 98% using normal chemical hence the material is cost effective. The solvent can be recovered after synthesis of the material which is further added advantages of the process. No requirement of any costly or sophisticated instruments for the synthesis of the material. Initially the adsorption increases on increasing pH but after a particular point, the adsorption remains constant. After optimization of pH time, studies have been done to check the effect of time on adsorption. Maximum absorption of Arsenic occurs within 30min at pH 6.5-7.5 and whereas Chromium occurs within 30min at pH 6.1-7.5. On further increasing time no significant changes has been observed. So the proposed material removes arsenic and chromium within 30 minutes efficiently and effectively. The purified water can be used for portable use as well as for other household utilities. For the purification of water contaminated by toxic metallic species like arsenic and chromium a simple, fast, low cost and non-toxic material has been presented. The material can be synthesized in bulk without help of any costly equipment. The material is of non-hazardous nature. The pH is the major deciding factor for quality of water, the proposed material do not altered even after adding and after removal of toxic contaminants like arsenic and chromium.

Scope: The proposed material can be safely used for water purification. The material will be beneficial for bulk purification of water. It can be impregnated in membrane form to make it commercial able in sophisticated water purification syst. This could further benefits army troops. They can carry few gram of propose material to purify the water of drain, ponds and river etc.

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