

REMOVAL OF FLUORIDE IONS IN DRINKING WATER USING Fe_2O_3 - ZnO NANOCOMPOSITE EMBEDDED WITH GRASS FIBRE

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ABSTRACT:

About 80% of the diseases in the world are due to poor quality of drinking water and the fluoride contamination in drinking water is responsible for 65% of endemic fluorosis in the world. Fluoride deficiency may cause dental caries and excessive use of its standard may cause dental disease, liver and skeletal fluorosis. In this present study, developing a Fe_2O_3 - ZnO embedded Acorus Calamus fibre catalyst to remove excess fluoride from Devipattinam drinking water. Using catalyst such as ZnO and Fe_2O_3 nanopowders which are mixed with pulverized raw grass powder. These carbon nanofibres were characterized by XRD and SEM. The derived nanocomposites were utilized for the removal of fluoride from the drinking water. The water sample was collected from Devipattinam and it was used for further analysis. The solution isotherm and kinetics experiments were performed by batch adsorption experiments and were carried out. The defluoridation studies were conducted for the optimization of various experimental conditions like contact time, initial fluoride concentration, adsorbent dose and fluoride uptake with fixed dosage by varying pH. The percentage of fluoride ion adsorption increases with increase in adsorbent dose. At a pH of 10 which gives the maximum fluoride adsorbent for metal oxide based fiber.

Keywords : *Fluorosis, Defluoridation, Nanocomposite, Carbon nanofibre.*

1. INTRODUCTION

Most of the diseases in the world are due to poor quality of drinking water and the fluoride contamination in drinking water is mainly responsible for endemic fluorosis in the world. Fluoride deficiency may cause dental disease, liver and skeletal fluorosis. Fluorosis is a slow, progressive, crippling malady, which affects every organ, tissue and cell in the body and results in health complaints having overlapping

manifestations with several diseases. The disease “fluorosis” has now become a global problem and the health impairment due to fluorosis has occurred in the citizens of about 25 nations across the globe and more than 200 million people worldwide are at the risk of fluorosis. WHO has determined 0.7 mg/L for optimum range of fluoride to reduce dental caries and avoid fluorosis in tropics and up to 1.2 mg/L in cold regions [1]. The fluorosis is caused by oral intake of fluoride when drinking water contains more than the

permitted concentration of fluoride. The most affected states in India are Rajasthan, Andhra Pradesh, Orissa, Gujarat, Madhya Pradesh and Chattisgarh states [2]. Dental fluorosis is a change in the appearance of the tooth's enamel surface. Most dental fluorosis is either very mild or mild. Forms of fluorosis appear as white, lacy markings on the tooth's enamel [3]. Intake of fluoride above 20 ppm may lead to severe toxicity like osteosclerosis (in which about 50% of OH group in $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ are replaced by F in bones). It leads to skeletal fluorosis and hyper calcification [4]. Zinc oxide was white crystalline powder which is nearly insoluble in water [5] [6]. It has wurzite structure with lattice spacing in nanometers [7]. This nanoparticles are useful as antibacterial and antifungal agents when incorporated into materials, such as surface coatings (paints), textiles, and plastics [5]. Due to bacteriostatic and fungistatic behavior of Zinc Oxide, it was well studied and utilized in personal care products. Due to its non-toxicity and compatibility with skin, makes it a suitable additive for textiles and surfaces that come in contact with human body [8]. ZnO are directly applied to the plastic films [9]. Iron oxide nanoparticles have one more special property in the form of super paramagnetism [10]. In the heavy metal separation, used this remediation technology and its capability to treat large volume of waste water, being convenient for magnetic separation make its potential application in water treatment [11].

2. MATERIALS AND METHOD

Sambu Grass (4.2g), Water sample (180 ml), ZnO nanopowder (0.7g), and Fe_2O_3

nanopowder (0.7g) are the essential materials used for this analysis and water sample was collected from Devipattinam. The sample was analysed for ions like fluoride, chloride, iron, magnesium. The study was particularly concentrated the removal of fluoride ion in water.

2.2. Processing of sambu Grass

Sambu Grass is a natural biofiber. The cleaned dry grass was pulverized and the fibrous powdered materials was washed well with doubly distilled water to remove the free acid, followed by thermal treatment using chemical vapour deposition (CVD) set up at a heating rate of $50^\circ \text{C}/\text{min}$ in the presence of flowing N_2 (250ml/min). The heating continued upto a final temperature at 300°C where it was held for 5 minutes, to obtain thermally activated carbon without using any catalysts. The resulting product was cooled to room temperature and sieved to the desired particle size. Finally the product was stored in vacuum desiccators until required for further experiments.

2.3. Preparation of ZnO

The preparation of ZnO is carried out by sol gel process at $800\text{-}900^\circ \text{C}$. Potassium hydroxide (1.12g) is dissolved in 10 ml of water. This KOH solution was added with zinc acetate dehydrate solution drop wise under continuous stirring. After few minutes the white solution was obtained, this mixture was further heated for 3 hours at 200°C without stirring. Then the suspension was centrifuged and then received product has washed with distilled water in an ultrasonic waterbath. The powder was dried at 70°C and characterized by XRD.

2.4. Preparation of Fe₂O₃

Fe₂O₃ was prepared by slow chemical reduction method. In this method Fe₂O₃ was mixed with de-ionized water and stirred for 20 minutes. pH level was adjusted to 7.0 with 5M NaOH solution. The Fe₂O₃ precipitate was filtered and washed with distilled water and then it was dried.

2.5. Fluoride determination

BaCl₂ was pipetted into the water sample, this solution was boiled and then cooled. The filtered solution was stirred with alizarin solution. pH was adjusted with HCl and NaOH. Lemon-yellow color solution was obtained, When we use acetic acid solution. Na₂S₂O₃ was added for the purpose of chloride ion removal. This obtained solution was titrated with thorium nitrate solution.

3. Result and discussion

3.1. Effect of contact time and initial fluoride concentration

S.No	T	Vol ume	Vol Th (No ₃) ₄	[F]		Indic ator
				Mol	g	
1	15	10	3.8	3.765×10 ⁻⁴	0.037	Aliz arin red
2	30	10	2.1	2.081×10 ⁻⁴	0.005	
3	45	10	1.9	1.882×10 ⁻⁴	0.052	
4	60	10	1.4	1.387×10 ⁻⁴	0.055	

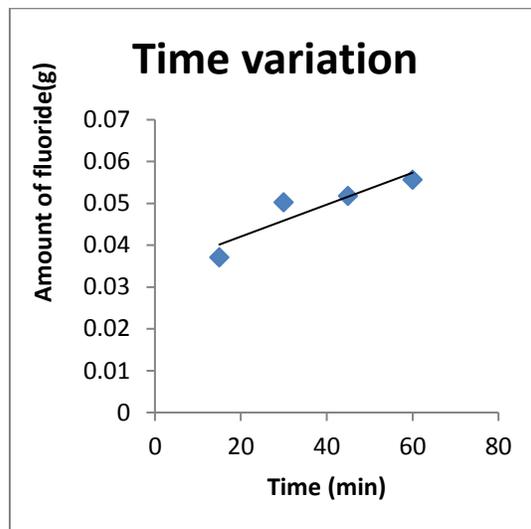


Figure 3.1 Amount of fluoride adsorption with time

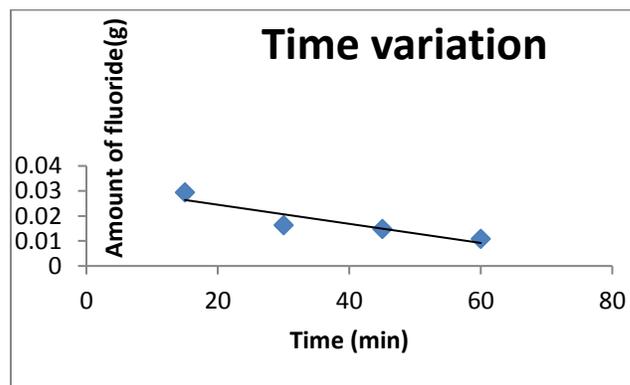


Figure 3.2 Amount of fluoride ion concentration in the sample solution with time

The adsorption of fluoride increases with time and gradually attains equilibrium after 60 minutes as shown in Fig.3.1. From this above figure, we have concluded 60 minutes was optimum contact time for defluoridation of the water sample. From figure 3.2. Further, it was observed that the concentration of fluoride ion continuously decreasing indicating the possibility of the formation of multilayers of fluoride ion at the pore volume and interface of the adsorbent.

3.2. Effect of Dose adsorbent and initial fluoride concentration

S.No	Dose Variation (g)	Volume of water sample	Volume of Th(NO ₃) ₄	Strength of fluoride ions		Indicator
				F ion (mole)	F ion (g)	
1	0.1	10	3.5	3.4685×10^{-4}	0.039	Alizarin red
2	0.15	10	2.6	2.5766×10^{-4}	0.046	
3	0.2	10	2.5	2.4775×10^{-4}	0.047	
4	0.25	10	2.3	2.2793×10^{-4}	0.048	
5	0.3	10	2.0	1.982×10^{-4}	0.051	
6	0.35	10	1.8	1.7838×10^{-4}	0.052	
7	0.4	10	1.5	1.4865×10^{-4}	0.054	

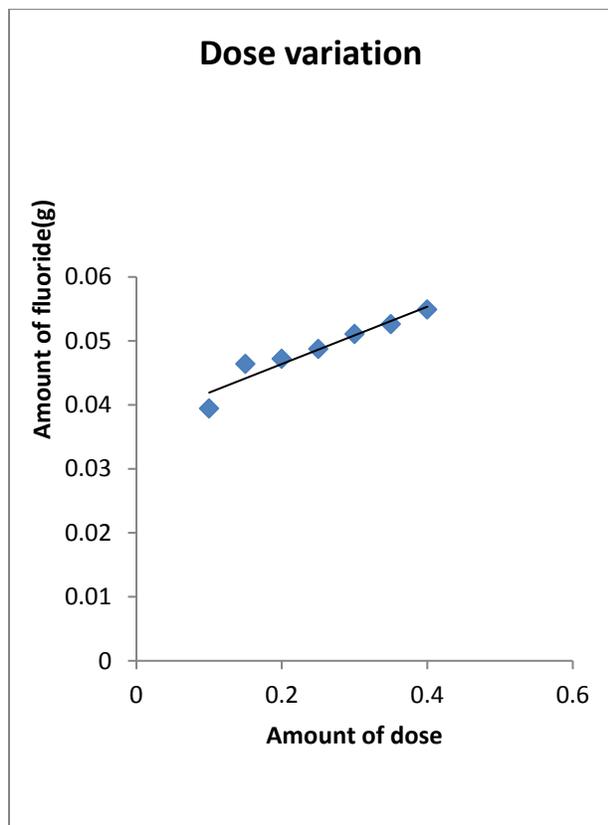


Figure 3.3 Amount of fluoride adsorption with Dose of catalyst

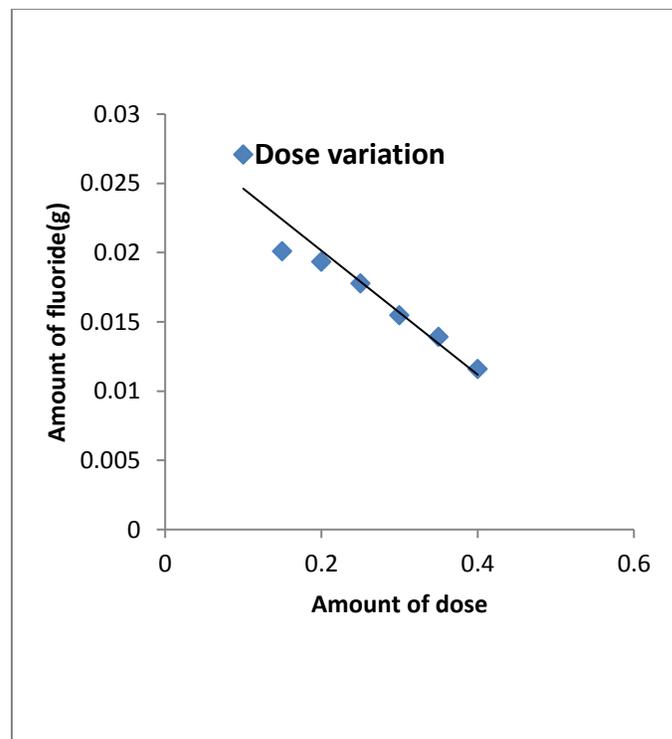


Figure 3.4 Amount of fluoride ion concentration in the sample solution with Dose

3.3. Effect of pH adsorbent and initial concentration

The percentage of fluoride ion adsorption increases with an increase in adsorbent concentration for all seven adsorbent doses, but after sometime, it gradually approaches a saturation value, denoting an equilibrium as shown in Figure 3.3. The effect of removal fluoride ions with dosage was examined by varying the adsorbent concentration from 0.1 g/100mL to 0.4 g/100mL while all other parameters were kept constant.

The adsorption of fluoride ions increase in pH for all five values. At pH of 10, this gives the maximum fluoride adsorption.

3.3. Effect of pH adsorbent and initial concentration

S. No	pH variation	Volume of water sample	Volume of Th (NO ₃) ₄	Strength of fluoride ions		Indicator
				F ion (mole)	F ion (g)	
1	4	10	43.2	4.281 1×10^{-3}	- 0.26	Alizarin red
2	5	10	6.2	6.144 2×10^{-4}	0.018	
3	6	10	4.3	4.261 3×10^{-4}	0.033	
4	7	10	3.2	3.171 2×10^{-4}	0.041	
5	8	10	3	2.973 $\times 10^{-4}$	0.043	
6	9	10	2.9	2.573 9×10^{-4}	0.044	
7	10	10	2.3	2.279 3×10^{-4}	0.048	

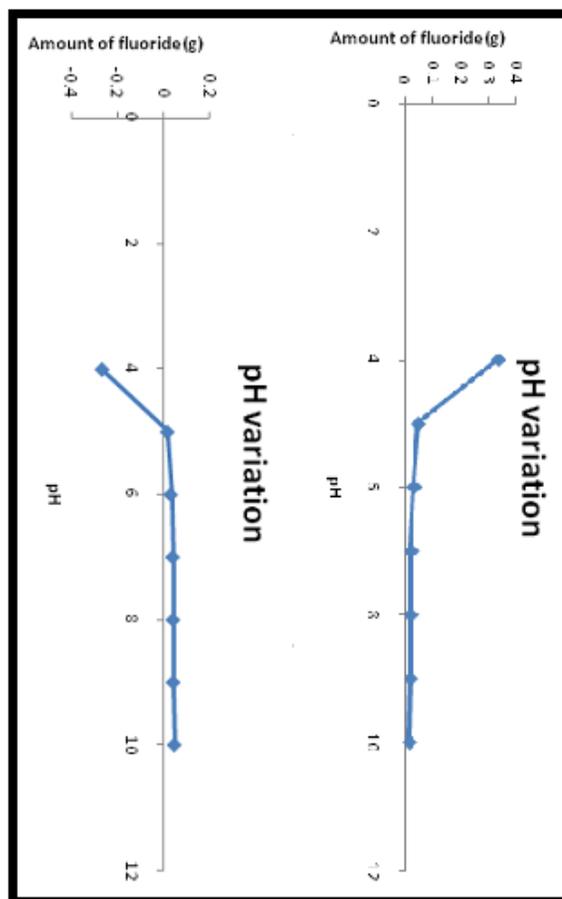


Figure 3.5 & Figure 3.6 Amount of fluoride variation with pH

3.4. X-Ray analysis

XRD was used to investigate the transformation in the phase structure of the nanofiber. For XRD measurements, metal adsorbed fibrous catalyst, which were collected on aluminum foils, were deposited on circular glass slides for further analyses. X-ray diffraction patterns were recorded using a Shimadzu XRD-6000 diffractometer. Scans were carried out from 10° to 30° at a scan rate of 2°/min using Ni-filtered CuK α radiation. The full width at half - maximum height (FWHM) of the diffraction peaks was calculated by fitting the X-ray diffraction data with a Gaussian-Lorentzian

function. The d-spacing for a given scattering angle was calculated by application of the Bragg equation.

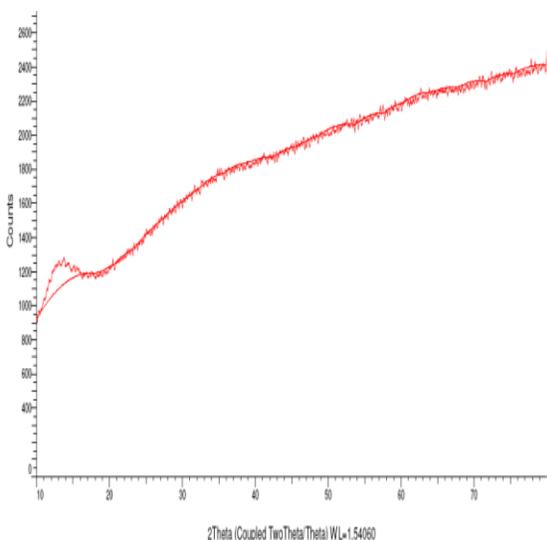


Figure 3.7. X-ray diffraction pattern of ZnO particle

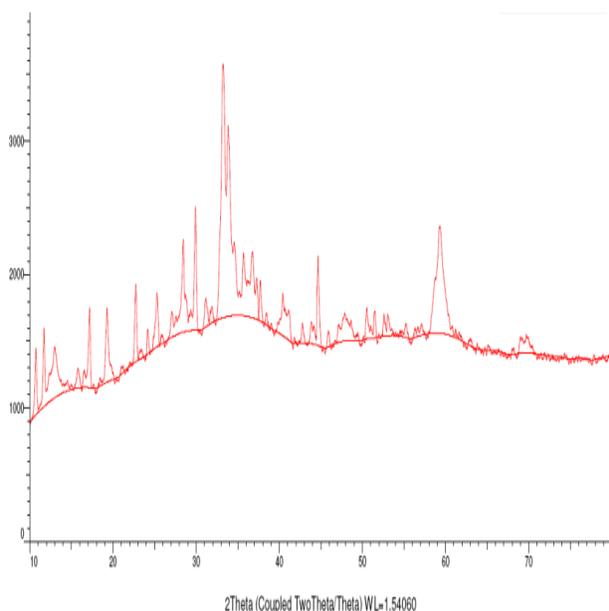


Figure 3.8 X-ray diffraction pattern of Fe₂O₃ particle

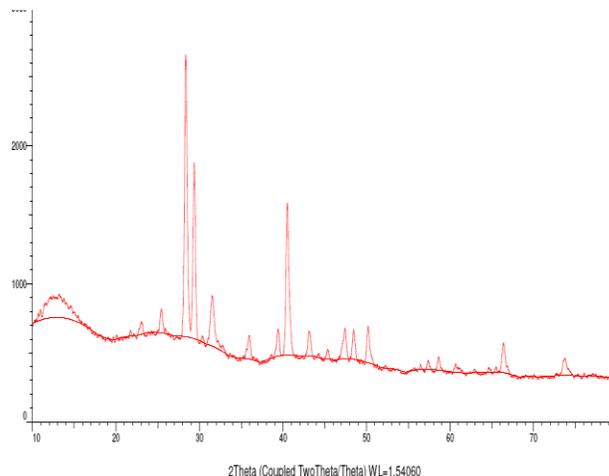


Figure 3.9 X-ray diffraction pattern of Fiber catalyst

The full width at half-maximum height of the diffraction peaks was calculated by fitting the X-ray diffraction data with a Lorentzian function and the crystallite size, was estimated by calculating the broadening of the diffraction peaks according to the Scherrer equation where δ is the Scherrer constant that depends upon lattice direction and crystallite morphology [11] and β is the full width at half-maximum height given in radians. These results indicated that the lignin nanofiber mats were converted to carbon nanofiber. This shows that metal catalysts are well adsorbed into the carbon nanofibre and can be used as effective catalyst.

4. Conclusion

Carbon nanofibers were prepared by thermal process and were characterized by XRD. Batch adsorption studies using the fluoride solution and with 1g of the adsorbent were carried out at 25°C-35°C. The adsorption of fluoride increases with time and gradually attains equilibrium, that particular time was known as contact time for defluoridation of the water sample. The percentage of fluoride

ion adsorption increases with increases the dose adsorbent, but after sometime, it gradually approaches a saturated value. The percentage of fluoride ions removal decreases with decrease in pH. At a pH of 10, this gives the maximum removal of metal oxide based fiber. As drinking water is usually the main source of fluorides intake, the levels of fluoride in tap water is very important in determining total fluoride exposure. The information of population about the levels of fluoride in drinking water is an important key element in health protection. Adequate information and recommendations help people themselves to make informed decisions and regulate health risks from drinking water. The results of the current study as well as other available data from water quality should be taken into account when developing strategies for safe drinking water supplies. Strategic plans and public awareness campaigns on fluorides in drinking water and health impact should be implemented.

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