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Research Article

EXTRACTION OF NITRITES FROM WASTE WATER USING BIO-SORBENTS DERIVED FROM *EICHHORNIA* PLANT

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ABSTRACT

Plant materials derived from ***Eichhornia plant*** have been probed for their sorption abilities towards Nitrites ions. Physicochemical parameters such as pH, agitation time and sorbent dosage have been optimized for the maximum extraction of Nitrites from polluted waters. Batch types of extraction methods have been adopted. Successful methodologies have been developed in removing more than 80% of Nitrites from simulated waters. Ten folds excess of common ions, except Sulphate, present in natural waters, show marginal interference. The procedures developed are successfully applied to the samples collected from polluted lakes.

Keywords: Nitrites, pollution control, bio-adsorbents.

1: INTRODUCTION

Nitrite is one of the dangerous polluting ions presents in waste waters. Its presence is attributed to the incomplete oxidation of nitrogenous organic matter in polluted waters. Further, Nitrite is used as a preservative for meat and to import aesthetic dark red color to the meet and this practice became the important source of Nitrite contamination[1-3].

Nitrite is highly toxic and it causes a disease called methemaglobinemia and subsequent cancer due its ability to form Carcinogenic nitrosamine and N-nitroso compounds with blood cells. More than half of the Cancer deaths in developed countries are due to Nitrite[2-7]. Nitrates and Nitrites are inter-convertible and anaerobic conditions reduce Nitrate to Nitrites[3, 8]. Recent research works suggest that Nitrite does not convert healthy cells into cancer cells but it stimulate the growth of cancer cells; the degree of stimulation depends upon various factors such as concentration of Nitrite and age and type of cancer cell.

In view of cancer prone epidemiological findings, many countries pass stringent laws to control the Nitrite prone cancer. The maximum permissible limits in waters are: EU: 0.5 ppm; USA: 1 ppm; China: 0.002 ppm in bottled waters.

There are some efforts to remove Nitrite from polluted waters[9-17]. De. D and Kalu[15] made kinetic studies of the electrochemical treatment of Nitrite and Nitrate ions on Iridium-modified Carbon Fiber Electrode. Saleem M et. al[17] studied electrochemical removal of Nitrite in simulated aquaculture. Katsuya Abe et al[18] investigated the aerial microalgae Trentepohlia aurea in relation to the removal characteristics of Nitrites. Polatides et al[19] studied the Electro chemical removal of Nitrate and Nitrite ions from aqueous solutions by pulsing potential electrolysis. A patent product under the brand name ALGONE is available for removal of Nitrites in the marine aquarium.

The methodologies based on bio-sorbents derived from agricultural wastes for the removal of polluting ions offer a potential alternative to the existing methods of detoxification and recovery of toxic and valuable ions in polluted waters[20-29]. In fact, these new novel biological approaches in the recent past have stimulated continuous and expanding research in developing eco-friendly procedures in the control of polluting ions[30-39].

This aspect of probing bio-sorbents is less trodden with respect to the control of Nitrites. Nes,e.Ozturk et al[20] investigated the removal of Nitrite from aqueous solution by adsorption using Sepiolite and powdered activated carbon.

While we are probing the affinity of different plants materials for their sorption abilities towards Nitrites, we noticed affinity between the Nitrites and sorbents derived from Eichhornia plant. The present work is a comprehensive study in optimizing the physicochemical parameters such as pH, sorbent dosage and agitation time, in developing an eco-friendly procedure for the quantitative removal of Nitrites from polluted water by effectively evoking the sorption nature of these sorbents.

2: METERIALS AND METHOD

(A): *CHEMICALS AND SOLUTIONS*: All Chemicals used were of analytical grade.

- **Stock Solutions of Nitrite**: 500 ppm stock was prepared using A.R. grade Sodium Nitrite and double distilled water and it is diluted as per the need.
- **Sulphanilic acid reagent**: 0.6 g of A.R. Sulphanilic acid was dissolved in 100 ml of 20% v/v hydrochloric acid.
- **α-Napthylamine reagent**: 0.48 g of A.R. α –naphthylamine was dissolved in 100 ml of 1.3 % v/v hydrochloric acid.
- **Sodium acetate, 2 M**: 16.4 g of anhydrous sodium acetate was dissolved in 100 ml of distilled water.

Fig. 1: Eichhornia: showing affinity towards Nitrites

(B): *ADSORBENTS:* Our pilot experiments revealed that plant materials of ***Eichhornia*** are found to be sensitive towards Nitrites. ***Eichhornia crassipes***, known as *common Water Hyacinth*, is an aquatic plant belonging to the family of Pontederiaceae and its habitant ranges from tropical desert to subtropical or warm temperate desert to rainforest zones.

The leaves and stems of ***Eichhornia crassipes*** were cut, washed with tap water followed by distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: < than 75 microns and activated at 105^{O} C in an oven and then employed in this study. Further these leaves were burnt to ashes and these ashes were also used in this work.

(C): ADSORPTION EXPERIMENT

The Batch system of extraction procedure was adopted[23, 24 & 40]. Carefully weighed quantities of adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500 ml /250 ml of Nitrite solutions of predetermined concentrations. The various initial pH values of the suspensions were adjusted with dil. HCl or dil. NaOH solution using pH meter. The samples were shaken in Mechanical shakers for a desired period and after the equilibration period, an aliquot of the sample was taken, filtered and the Nitrite content in it is determined spectrophotometrically[41].

Estimation of Nitrites

A measured quantity of the Nitrite sample was taken in to a 50 ml volumetric flask. To it 1 ml of Sulphanilic acid reagent solution was added, mixed well and was allowed to stand at least 3 min and not more than 10 min at room temp in diffused light. Then 1 ml of the α-Napthylamine solution and 1 ml of 2M-Sodium acetate solution to act as buffer (pH: 2.0-2.5) were added. The solution then diluted to 50 ml and mixed well. After 10 min, but not later than 30 min, the Optical Density of the reddish-purple color developed was measured at 520 nm against blank using U.V and visible spectrophotometer (Systronics make). Previously, a standard graph was constructed between O.D. and known concentrations of Nitrite, in conformation of Beer’s law adopting Least Square Method for linear graphs. The measured O.D. values for the unknown solutions were referred to standard graph to determine the concentrations of Nitrite in un-known samples.

(D): EFFECT OF INTERFERING IONS

The interfering ions chosen for study are the common ions present in natural waters, viz., phosphate, sulphate, fluoride, chloride, carbonate, calcium, magnesium, copper and zinc. The

synthetic mixtures of Nitrite and one of the interfering ions were so made that the concentration of the interfering ions maintained at tenfold excess than the Nitrate ion concentration.

500 ml of these solutions were taken in stopped bottles and then correctly weighed optimum quantities of the promising sorbents were added. Optimum pH was adjusted with dil. HCl or dil. NaOH using pH meter. The samples were shaken in shaking machines for desired optimum periods and then the samples were filtered and analyzed for Nitrites. % of extraction was calculated from the data obtained. The results are presented in the Table No. 1

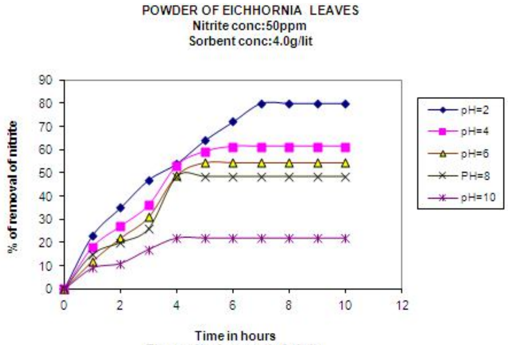
(E): APPLICATIONS OF THE DEVELOPED BIO-SORBENTS

The workability of the developed bio-sorbents for removing Nitrite ion concentrations in naturally occurring polluted waters were tried. For this purpose, five samples were collected from five lakes polluted with Nitrite at different places in Bapatla Mandalam of Guntur Dt of Andhra Pradesh and the actual concentration of Nitrite present in them was analyzed. Then these samples were subjected to the extraction of Nitrites using the bio-sorbents developed in this work at optimum conditions of pH, equilibration time and sorbent concentration. The results obtained were presented in the Table 2.

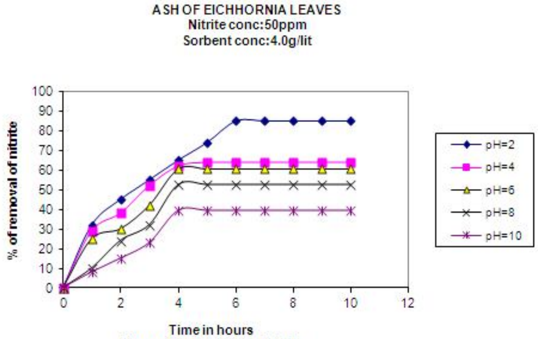
3: RESULTS AND DISCUSSION

The extraction characteristics of leaves, stems and their ashes of ***Eichhornia crassipes*** *towards Nitrites at varying physicochemical parameters* such as pH, time of equilibration and sorption concentration are presented ***in the Graph No. A: 1-3; B: 1 & C: 1.*** the following observations are significant:

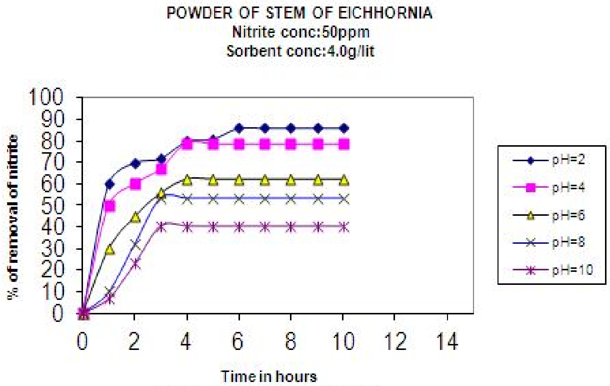
1. Percentage of extractability of Nitrite increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability remains constant, i.e. an equilibrium state has been reached (vide Graph Nos: A: 1-3).



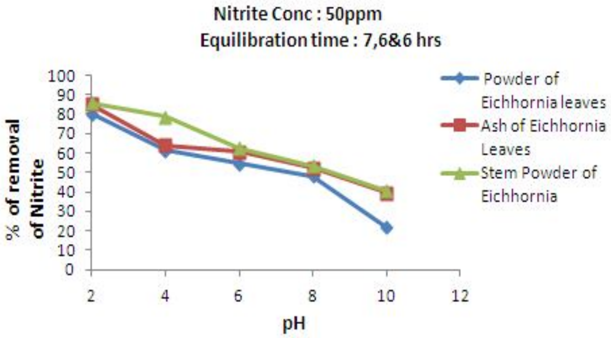
Time vs % of removal of nitrite
Graph No:A-1



Time vs % of removal of nitrite
Graph No:A-2



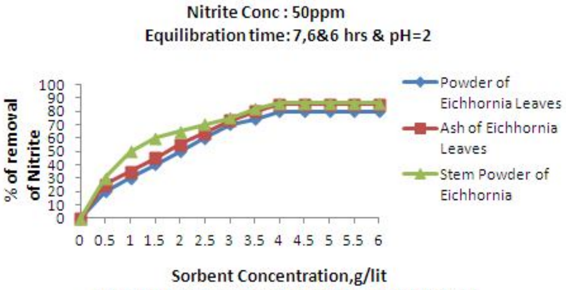
Time vs % of removal of nitrite
Graph No:A-3



pH Vs % of removal of Nitrite
Graph No:B-1

2. **pH sensitivity**: The % of extraction is found to be pH sensitive. The % of extractability of Nitrite increases with decreases in pH conditions of agitating solution for a fixed adsorbent concentration. (Vide Graph Nos : A: 1-3; B: 1). As for example, in the case of ***leaves powders of Eichhornia***, the maximum extractability is found to be : 21.8% at pH:10, 48.3% at pH:8; 54.5% at pH:6; 61.2% at pH:4 and 80.0% at pH:2. In the case of ***leaves ash of Eichhornia***, the maximum extractability is found to be : 39.3% at pH:10; 52.3 % at pH:8; 60.4% at pH:6; 63.8% at pH:4 and 85.0% at pH:2. In the case of ***stem powder of Eichhornia***, the maximum extractability is found to be: 40.6% at pH: 10, 53.5% at pH: 8; 62.4% at pH: 6; 78.5% at pH: 4 and 86.0% at pH: 2.
3. The extraction of Nitrite is found to be more in the case of bark powders as sorbents than ashes and powders of leaves. Further, the time needed for maximum removal of Nitrite is also found to be less in the case of bark powders and ashes of leaves than powders of leaves. As for example, the maximum extractability of Nitrite is 80.0% percent at pH: 2 after an equilibration period of 7 hrs. for Eichhornia leaves powders while with its ash of leaves, the extractability is found to be enhanced to 85.0% at pH:2 after an equilibration period of only 6 hrs. And with its stem powders, the extractability is found to be enhanced to be 86.0% at pH:2 after an equilibration period of only 6 hrs. ***With stem powders as sorbents more than 70% extraction is observed even at 2.0 hrs of extraction***.
4. When percentage removal is studied with respect to adsorbent dosage at fixed optimum pH: 2 and at optimum equilibration times, the graphs increase up to certain dosage and from then onwards plateaus are obtained. (Vide Graph No. C: 1).

   With powders of leaves, ashes of leaves and with the powders of stems, the optimum sorbent dosage is found to be 4g/lit for Eichhornia. (Vide Graph No:: C:1).



Sorbent Concentration Vs % of removal of Nitrite

Graph No:C-1

5. **Interfering Ions**: The extractions of Nitrite ions in presence of tenfold excess of common ions found in natural waters, namely, Chloride, Fluoride, Carbonate, Sulphate, Phosphate, Calcium, Magnesium, Copper and Zinc ions, have been studied. Except Sulphate, the other ions chosen for study have shown marginal interference at the optimum conditions of extraction as cited in the Table No.1.

DISCUSSIONS

The affinity the sorbents towards Nitrite may be due to the naturally occurring surface functional groups like OH/COOH groups present in these lingo celluloses' materials. The dissociation or association depends upon pH conditions. At high pH values, these groups dissociates as:

$$\text{Adsorbent-OH} \rightleftharpoons \text{Adsorbent-O}^- + H^+$$

$$\text{Adsorbent-COOH} \rightleftharpoons \text{Adsorbent-COO}^- + H^+$$

and imparts weak cation exchange ability and at low pH values, the dissociation is less favored and protination may also occur:

$$\text{Adsorbent-OH} + H^+ \rightleftharpoons \text{Adsorbent-}\underset{H}{O^+}H \quad ,$$

resulting weak anion-exchange ability. This is reflected in sorption of Nitrite. Nitrite being an anion is adsorbed by these materials at low pH values and hence the high % of removal. At high pH values cation affinity persists and not anion and hence, Nitrite anion show low % of removal. The decrease in the rate of sorption with the progress in the equilibration time may be due to the more availability of sorption sites initially and are progressively used up with time due to the formation of adsorbate, Nitrite, film on the sites of the sorbent and thus resulting in decrease in sorption ability.

4. APPLICATIONS

Sample waters at five lakes polluted with Nitrite ions have been collected and the successful sorbent developed in this work have been tried for the removal of Nitrite ions at optimum conditions of extraction. It is found that the sorbents developed in this work are successful in removing Nitrites considerably in these samples of water at optimum conditions of pH, equilibration time and sorbent dosage. % removal of Nitrite in these samples of water is found to be: 74.5 % to 79.5% with leaves powder of Eichhornia ; 81.9% to 85.5% with the stem powders of Eichhornia ; and 80.0% to 85.0% with the leaves ashes of Eichhornia (vide Table 2).

Table 1: Effect of Interfering Ions on the Extraction of Nitrite From Simulated Waters

S. No.	**Interfering ions : in tenfold excess**	**% of Extractability of Nitrite: Conc. Of Nitrite:50 ppm**		
		Eichhornia Plant		
		Thermally activated Leaves powder of size < 70µ; at pH:2; Eq. time: 7.0 hrs; Sorbent Conc.: 4.0 g/l	***Thermally activated Stems powders of size < 70µ;at pH: 2; Eq. time: 6.0 h; Sorbent Conc. 4.0 g/l***	***Leaves ash; pH: 2; Eq. time: 6.0h; Sorbent Conc.:4.0 g/l***
1	Without interfering ions	80.0%	86.0%	85.0%
2	$SO4^{2-}$	65.6%	69.0%	71.0%
3	Phosphate	78.5%	80.5%	81.5%
4	Carbonate	77.5%	82.2%	83.5%
5	Chloride	76.8%	82.5%	82.5%
6	Fluoride	75.8%	81.5%	82.0%
7	Ca^{2+}	78.5%	83.0%	80.0%
8	Mg^{2+}	79.5%	83.5%	82.5%
9	Cu^{2+}	80.0%	81.5%	84.0%
10	Fe^{2+}	77.5%	83.5%	82.8%
11	Zn^{2+}	79.8%	84.5%	83.5%
12	Ni^{2+}	77.8%	85.0%	85.0%

Table 2: Percentage of Extraction of Nitrites from Polluted Water Samples Using Bio-Sorbents Developed in This Work

Different Samples (Conc. Of Nitrite found is shown in the parenthesis)	**% of Extractability of Nitrite**		
	Eichhornia Plant		
	Thermally activated Leaves powder of size < 70µ; at pH:2; Eq. time: 7.0 hrs; Sorbent Conc.: 4.0 g/l	***Thermally activated Stems powders of size < 70µ;at pH: 2; Eq. time: 6.0 h; Sorbent Conc. 4.0 g/l***	***Leaves ash; pH: 2; Eq. time: 6.0h; Sorbent Conc.:4.0 g/l***
Simulated waters (50nppm)	80.0%	86.0%	85.0%
Sample: 1:(4.5 ppm)	78.6%	83.5%	82.5%
Sample: 2 (5.5 ppm)	79.5%	82.5%	81.2%
Sample: 3 (6.2 ppm)	76.5%	85.5%	82.5%
Sample: 4 (7.0 ppm)	75.5%	84.0%	83.0%
Sample: 5(7.5 ppm)	74.5%	82.5%	82.0%
Sample: 6 (8.0 ppm)	77.0%	81.9%	80.0%

5. CONCUSSIONS

1. Thermally activated powders of leaves or stems or ashes of Eichhornia have been found to have strong affinity towards Nitrites at low pH values.
2. % of removal of Nitrite is pH sensitive and also depends on sorption concentration and time of equilibration
3. Ten folds excess of common ions present in natural waters, viz., Cl^- , F^-, Phosphate, Carbonate, Ca^{2+}, Mg^{2+} , Cu^{2+} , $Fe^{2+}$and Zn^{2+} have less affected the % of extraction of Nitrite at optimum conditions of pH , equilibration time and sorbent concentration. Sulphate interfered but % percentage of extraction never comes down 65.6%.
4. We claim 80%, 86% and 85% removal of Nitrite with the activated leaves powders, stem powders and ashes of leaves of ***Eichhornia plant*** as biosorebents respectively at optimum extraction conditions.
5. The methodologies are successfully applied to water samples collected from polluted lakes.

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