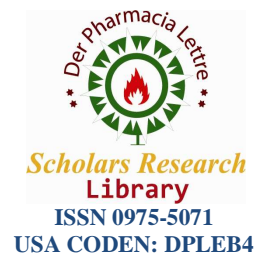




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Extraction of nitrite ions from polluted waters using ash of *Tridax procumbens* leaves as adsorbent

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ABSTRACT

Nitrite is highly toxic and is found in sewage and sanitary wastes from humans and animals due to the incomplete oxidation of nitrogenous organic matter. The methodologies for removing this health hazard have environmental significance. In the present work, a low cost bio-sorbent is developed from the ash of *Tridax procumbens* plant leaves to remove nitrites from polluted waters using batch adsorption methods. The conditions for the maximum extraction of nitrite using the bio-sorbent are optimized by varying the physicochemical parameters such as pH, contact time, initial nitrite ion concentration and adsorbent dosage. The effect of co-ions commonly present in water on the % of removal is also studied. Freundlich as well as Langmuir isotherms are plotted and correlation coefficient (R^2) value confirmed that the adsorption follows the Langmuir isotherm indicating formation of monolayer on the surface of adsorbent. Pseudo-first-order and pseudo-second-order models are applied to identify the rate and kinetics of adsorption process. The adsorption process has good correlation coefficient value with pseudo-second-order model. The procedure developed is applied to real ground water samples and found to be successful.

Key words: Nitrite pollution, adsorption, ash of *Tridax procumbens* leaves, application

INTRODUCTION

Pollution of water resources by excessive presence of nitrogen compounds such as nitrate, nitrite and ammonium, is a real health and environmental problem. Excessive levels of these nitrogen compounds in drinking water have caused serious illness and sometimes death in infants less than six months of age. This condition results when nitrate is converted to nitrite in the infant's body. Nitrite then interferes with the oxygen carrying capacity of the blood and cause blue disease in babies called methemoglobinemia in newborn infants as well as other illnesses [1]. Symptoms include shortness of breath and blueness of the skin. This is an acute disease in which symptoms can develop rapidly in infants from very minor exposure. The U.S. Environmental Protection Agency [2] has established maximum contaminant levels of 10 mg/lit for nitrate and 1.0 mg/lit for nitrite.

Nitrite levels can become elevated when the surrounding area is heavily developed, used for agricultural purposes, or subject to heavy fertilization. The heavy utilization of artificial fertilizers and the uncontrolled discharges of raw have been known to cause the penetration of large quantities of nitrogen and phosphate compounds into the ground and surface waters [3-6].

The most important environmental problems caused by nitrogen and phosphorus compounds are eutrophication of water supplies and infectious disease [7]. These components which are involved in the eutrophication of surface waters and the presence of high levels of nitrate and nitrite ions in drinking water has an adverse risk to human health [8-11].

Several purification techniques are used to remove or reduce the amount of toxic pollutants found in water and wastewater. These include methods of ion exchange, biological treatment, reverse osmosis, electrodialysis, membrane separation and adsorption [12-15]. Adsorption process is considered to be most suitable and widely used technique because of its simple operation and availability of wide range of efficient and economical adsorbents.

The use of agricultural waste products as bio-sorbents 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 [16- 24]. Parimala et al., [25] explored the use of low cost agricultural wastes as sorbents for the control of nitrites. Our research group is investigating on these bio-methods and successful methodologies have been developed in controlling some potential pollutants [26- 32].

In the present work, the removal of nitrite from aqueous solution by adsorption process has been studied using ash of *Tridax procumbens* plant leaves as bio-adsorbent. The performance of the said adsorbent has been evaluated under batch conditions of extraction by varying the various physicochemical parameters such as pH, contact time, adsorbent dose, initial concentration of the nitrite ion and effect of interfering ions. The extraction conditions have been optimized for the maximum removal of nitrites from waters. Further, the nature of the adsorption process has been analyzed by Freundlich and Langmuir isotherms and kinetics of adsorption have been studied using pseudo first-order, pseudo second-order models. The methodologies developed have been applied to real ground water samples polluted with nitrite.

MATERIALS AND METHODS

2.1. Materials

2.1.1 Reagents and chemicals

All the chemicals used were of Analytical Reagent grade purchased from Merck. India Pvt. Ltd. and Sd. Fine Chemicals and all solutions were prepared by using double distilled water through- out this study. Nitrite stock solution of 500 mg/lit was prepared by dissolving requisite amount of Sodium Nitrite in double distilled water and the required working standards were prepared by successive quantitative dilution of the stock solution. Sulphanilic acid reagent, α -Naphthylamine reagent and Sodium acetate (2M) were prepared as described in Standard methods for the Examination of Water and Waste water [33].

2.1.2 Plant selected for the study

Our preliminary work shows that *Tridax procumbens* plant has affinity towards Nitrite ions. In this work the adsorbent derived from this plant has been probed for the removal of Nitrite ions from polluted waters.



Figure 1: *Tridax procumbens* plant

Tridax procumbens (Figure 1), commonly known as coatbuttons or tridax daisy is a species of flowering plant in the Asteraceae family. It is best known as a widespread weed in gardens, in waste places and along the roadsides and pest plant. Traditional medicines can be prepared from the all parts of this plant.

2.1.3 Adsorbent preparation

The bio-sorbent was prepared from leaves of *Tridax procumbens* plant by initial cleaning of dust particles with double distilled water and dried completely under sunlight. The dried leaves were burnt to ash and sieved into desired particle sizes and this ash was employed in this work.

2.2. Methods

2.2.1 Batch mode adsorption studies

The batch method of extraction procedure was adopted [17, 19, 34]. 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 [35].

2.2.1 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 -Naphthylamine 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 concentration of nitrite in un-known samples.

2.2.2 Nitrite ion analysis

The percentage removal of nitrite ion and amount adsorbed (in mg/g) were calculated using the following equations.

$$\% \text{ Removal (\% R)} = \frac{(C_i - C_e)}{C_i} \times 100$$

$$\text{Amount adsorbed (q}_e\text{)} = \frac{(C_i - C_e)}{m} \times V$$

where C_i = initial concentration of the nitrite solution in mg/lit
 C_e = equilibrium concentration of the nitrite solution in mg/lit
 m = mass of the adsorbent in grams
 V = volume of nitrite test solution in liters

RESULTS AND DISCUSSION

3.1 Effect of various physicochemical parameters on nitrite removal

3.1.1 Effect of dosage:

The effect of adsorbent dosage on the nitrite removal efficiency was studied with increasing adsorbent dosage from 0.5 to 5.0 g/lit keeping all other parameters constant at optimum levels namely, nitrite ion concentration: 50 mg/lit, pH: 2 and contact time: 5 hrs. The obtained results were plotted and shown in Figure 2.

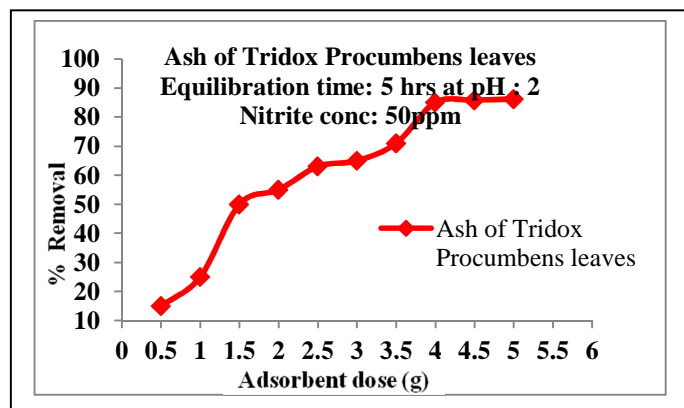


Figure 2: Effect of dosage on nitrite removal

As is seen from the plot that the removal of nitrite ion increases with an increase in the adsorbent dose and attained maximum removal at 4.0 g/lit and then onwards, there is no further removal of nitrite with increase of the adsorbent dose.

The increase in removal with increase in dosage may be attributed to the increasing availability of number of active sites. After certain dosage, the adsorbed adsorbate ions may either block the access to the internal pores of adsorbent or may cause particles to aggregate and thereby minimizing the availability of active sites for adsorption.

The percentage removal of nitrite is found to be insignificant after a dose of 4.0 g/lit and hence, this has been fixed as optimum dosage of adsorbent.

3.1.2 Effect of pH:

The effect of pH on the removal of nitrite ion from aqueous solution was studied by varying the pH from 2 to 10 under optimum parameters i.e. with a solution of 50 mg/lit of nitrite ion concentration, contact times of 5 hrs, dose of 4.0 g/lit. The results obtained were plotted as percentage removal of nitrite ion versus pH as shown in Figure 3.

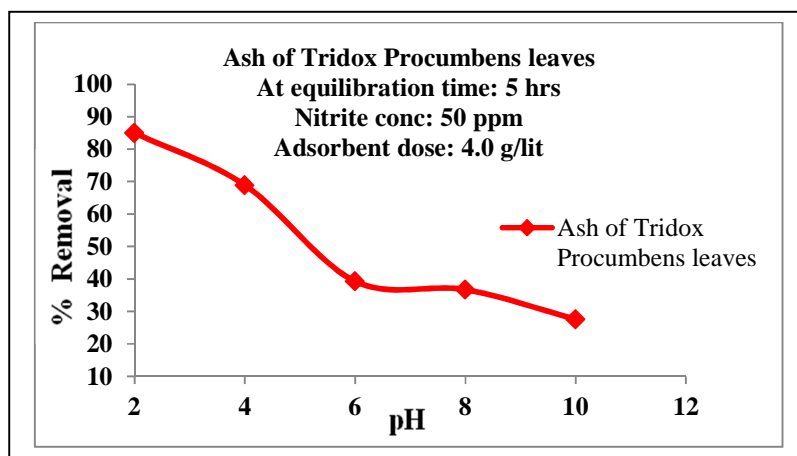


Figure 3: Effect of pH on nitrite removal

The percentage of extraction is found to be pH sensitive. With the increasing pH, extractability of nitrite decreases for a fixed adsorbent concentration. The lingo celluloses' materials have -OH/COOH groups and their dissociation is pH dependent. At high pH values, these groups dissociates and imparts weak cation exchange ability and at low pH values, the dissociation is less favored and protination may also occur and resulting weak anion-exchange ability.

This is reflected in sorption of nitrite. Nitrite being an anion is adsorbed by the adsorbent at low pH values and hence the high percentage removal. At high pH values, cation affinity persists and not anion and hence, nitrite anion show low percentage removal. The maximum extraction, 85 %, has been found to be at pH: 2.

3.1.3 Effect of contact time:

The adsorption experiments were conducted at optimum conditions of pH: 2.0, nitrite concentration: 50 mg/lit, sorbent dosage: 4.0 g/lit with varying the contact time from 10 to 100 min. The results obtained were plotted as percentage removal of nitrite ion Vs contact time in hours as shown in Figure 4.

As contact time increases, initially the percentage removal of nitrite ion increases rapidly because of the availability of more active sites on the surface of the adsorbent [36] and after certain time approached an almost constant because of the availability of active sites on the surface of the adsorbent decreases. From the observed results, the optimum contact time of adsorbent is 5 hours.

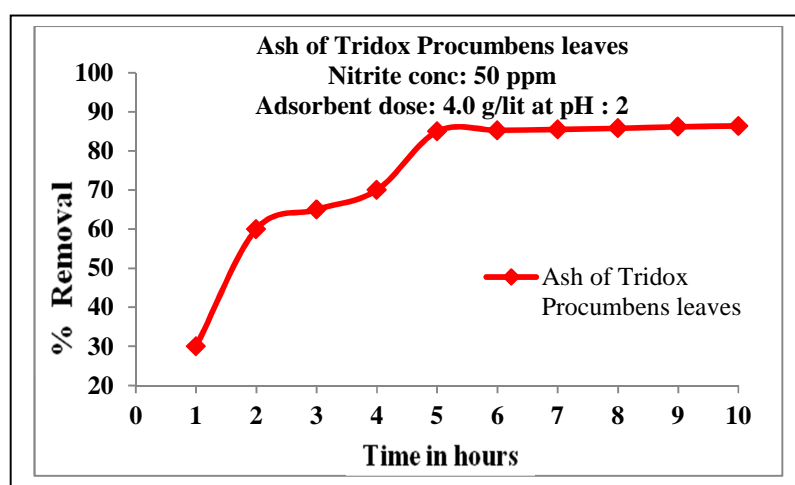


Figure 4: Effect of contact time on nitrite removal

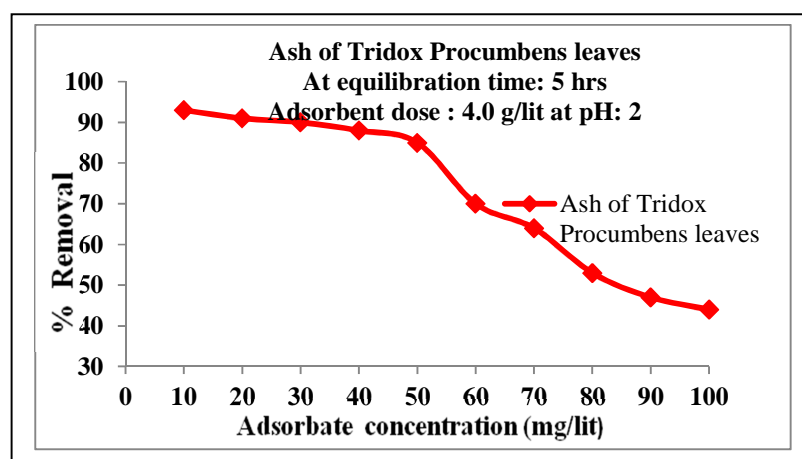


Figure 5: Effect of initial concentration on nitrite removal

3.1.4 Effect of initial concentration:

The effect of initial concentration on extent of removal of nitrite ion from aqueous solution was studied by varying the initial concentration of nitrite ion solution from 10 to 100 mg/lit under constant parameters i.e. at a fixed pH = 2, contact times of 5 hrs with a dose of 4.0 g/lit. The results obtained were plotted as percentage removal versus initial concentration of nitrite ion solution as shown in Figure 5.

It was noticed that the percentage removal of nitrite gradually decreased with increasing nitrite concentration. This might be due to the fact that for a constant adsorbent dosage, total available adsorption sites were limited and hence, insufficient numbers of active sites are available on the adsorbent surface to accommodate nitrite ions at high concentrations of nitrite ions [37-38]. With an increase in initial concentration of nitrite ion solution from 10 to 100 mg/lit, the percentage removal (% R) decreased from 93.0 to 44.0 %.

3.1.5 Effect of interfering ions:

The effect of interfering anions such as phosphate, sulphate, fluoride, chloride, carbonate, calcium, magnesium, copper and zinc was examined at five fold excess of interfering ions keeping all other parameters constant: at pH: 2, nitrite ion concentration: 50 mg/lit, adsorbent dosage: 4.0 g/lit, contact time: 5 hrs. The results obtained were presented in Table 1.

The interfering ions, commonly present in natural waters, viz., phosphate, sulphate, fluoride, chloride, carbonate, calcium, magnesium, copper and zinc show less effect on the extractability of nitrite ions at the optimum conditions of pH, equilibration time and sorbent dosage.

Table 1: Effect of interfering ions on nitrite removal

Adsorbent	Maximum Extractability (%)
Ash of <i>Tridax procumbens</i> leaves	85.0 (Nitrite conc: 50 ppm, pH: 2, 5.0 hrs, 4.0 g/lit)
Interfering ions	Extractability of nitrite in presence of fivefold excess of (250 ppm) interfering ions at optimum conditions (Nitrite conc: 50 ppm, pH: 2, 5.0 hrs, 4.0 g/lit).
SO ₄ ²⁻	82.5
PO ₄ ³⁻	80.3
Cl ⁻	82.2
CO ₃ ²⁻	80.9
F ⁻	81.4
Ca ²⁺	82.5
Cu ²⁺	81.8
Zn ²⁺	82.8
Mg ²⁺	83.4

3.2 Adsorption Isotherms:

Adsorption isotherms are studied to evaluate the relation between the adsorbate concentrations remaining in the bulk solution to the amount of adsorbate adsorbed at the solid/solution interface. Two well known models, Freundlich [39] and Langmuir [40] adsorption isotherms have been selected for describing adsorption isotherms at a constant temperature.

Linear form of **Freundlich** isotherm equation is $\log (q_e) = \log k_F + \left(\frac{1}{n}\right) \log C_e$

Linear form of **Langmuir** isotherm equation is $(C_e/q_e) = (a_L/k_L) C_e + 1/k_L$

where, k_F and $1/n$ are the Freundlich constants, C_i is the initial nitrite ion concentration, q_e (mg/g) is the amount of nitrite ions adsorbed per unit weight of the adsorbent (mg/g), k_L and a_L are the Langmuir constants related to capacity and energy of adsorption, respectively and k_L/a_L is the theoretical monolayer saturation capacity, q_m . The correlation coefficient (R^2) value is used to judge the most fitted model and the Langmuir isotherm with higher correlation coefficient value is best-fitted to the process with monolayer coverage and homogeneous adsorption of nitrite on the surface of adsorbents. The plots and values of the Freundlich and Langmuir adsorption isotherm constants together with the correlation coefficients values were presented in Figure 6 and Table 2 respectively.

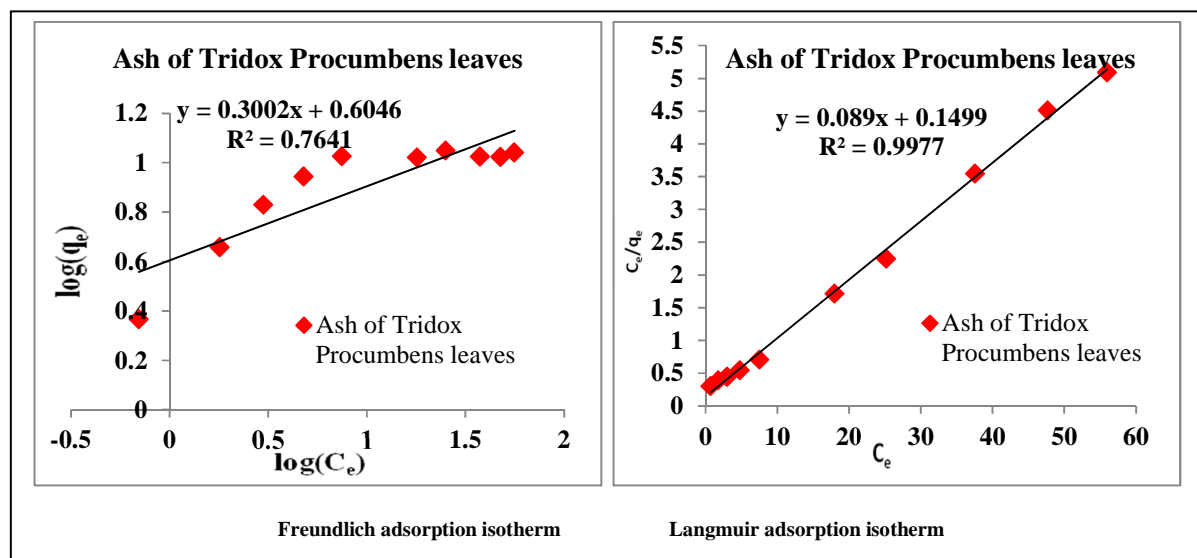


Figure 6: Freundlich and Langmuir adsorption isotherms

3.3 Kinetic study of adsorption:

To study the rate and kinetics of adsorption of nitrite ion on to the adsorbent some kinetic models namely pseudo first-order [41-43] and pseudo second-order models [42-44] are discussed.

The **pseudo-first order** model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites.

Its linearized equation is expressed as: $\log(q_e - q_t) = \log(q_e) - (k_1/2.303) t$

q_e = the amount of adsorbed adsorbate at equilibrium, (mg/g)

q_t = the amount of adsorbed adsorbate at time t , (mg/g)

k_1 = the pseudo first-order rate constant, (min^{-1})

The **pseudo second-order model** is based on the assumption that the adsorption involving valence forces through sharing or exchange of electrons between adsorbate and adsorbent.

Its linearized equation is expressed as: $(t/q_t) = (1/k_2 q_e^2) + (1/q_e) t$

k_2 = the pseudo second-order rate constant, (g/mg.min)

The correlation coefficient (R^2) value was used to find the best-fit model and the R^2 value close to unity indicates the applicability of the adsorption kinetics.

The correlation coefficient value for the pseudo second-order model is greater than the pseudo first-order model and this indicates that the pseudo second-order model is the best fit to the experimental data of the present studied adsorption system.

The plots and values of pseudo first-order and pseudo second-order model constants together with the correlation coefficients values were presented in Figure 7 and Table 2 respectively.

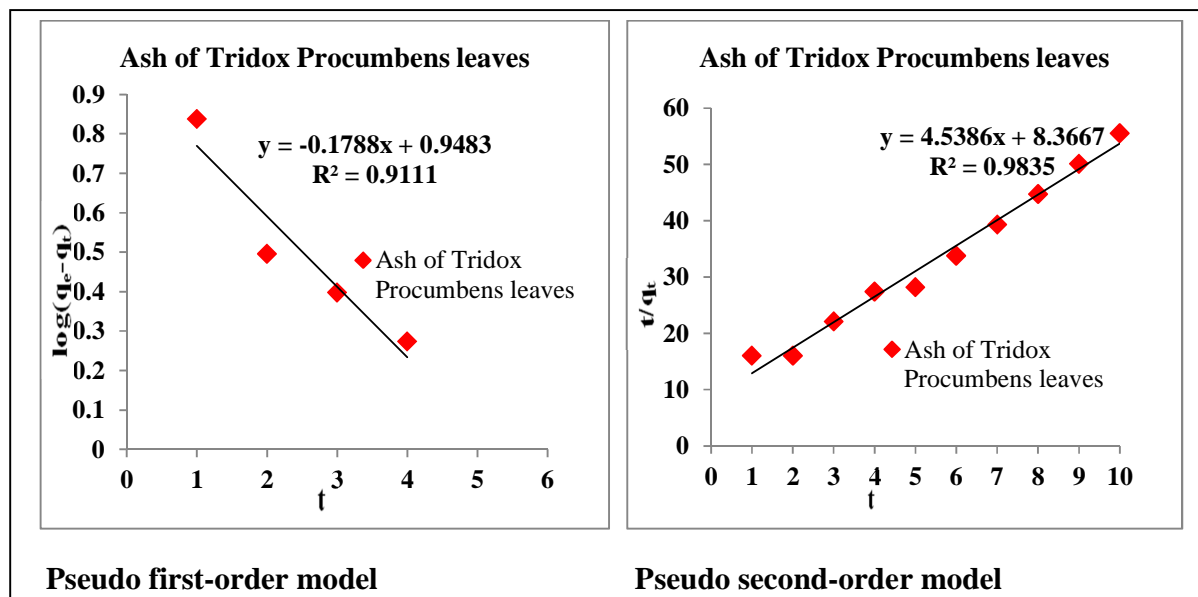


Figure 7: Pseudo first-order and Pseudo second-order models

Table 2: Adsorption and kinetic parameters

S.NO.		Slope	Intercept	R ²
1	Freundlich isotherm	0.3002	0.6046	0.7641
2	Langmuir isotherm	0.0890	0.1499	0.9977
3	Pseudo first-order model	-0.1788	0.9483	0.9111
4	Pseudo second-order model	4.5386	8.3667	0.9835

4. APPLICATIONS:

The methodology developed in this work with the new adsorbent for removal of nitrite ion is applied to the real water samples collected from ground waters in nitrite affected areas in Bapatla Mandal of Guntur District of Andhra Pradesh.

Five water samples are collected from nitrite polluted areas and the adsorbent studied in this work is tried for the removal of nitrite ions at optimum conditions of extraction. It is found that the adsorbent developed in this work is successful in removing nitrite ions from polluted samples of water at optimum conditions of pH, equilibration time and sorbent dosage. The results obtained are presented in the Table 3.

Table 3: Percentage of extractability of nitrites in polluted water samples

S. No.	Water samples	C _i (mg/lit) (initial concentration of nitrite)	C _f (mg/lit) (concentration of nitrite after removal)	% Removal
1	Sample 1	4.2	0.820	80.4
2	Sample 2	3.8	0.789	79.2
3	Sample 3	4.7	0.812	82.7
4	Sample 4	4.4	0.910	79.3
5	Sample 5	5.1	0.889	82.5

From the Table it is observed that the concentration of nitrite in all the polluted water samples collected from different areas of Bapatla Mandal, Guntur Dist. is varied from 3.8 to 4.7 mg/lit which is beyond the permissible limit by USEPA: 1.0 mg/lit [2].

After removal of nitrites from polluted water samples using the adsorbent, the concentration of nitrite is below the permissible limit under optimum experimental conditions. Thus the methodology developed in this work using the new adsorbent is remarkably successful.

CONCLUSION

In this study, it is concluded that a low cost bio-sorbent is developed from the ash of *Tridax procumbens* leaves to remove nitrite ions from polluted waters. The optimum conditions for the maximum extraction (85 %) of nitrite ions from waste are: pH: 2, contact time: 5 hrs, sorbent dosage: 4.0 g/lit with nitrite ion concentration: 50 mg/lit. The common ions naturally present in waters show marginal effect on the percentage of extraction.

The mechanism of the adsorption process is confirmed as monolayer formation because it follows the Langmuir isotherm and the kinetics of the process is fitted to the pseudo second-order kinetics.

The bio-sorbent developed in this work is successfully applied to real ground water samples collected from Bapatla Mandal of Guntur Dist of Andhra Pradesh. The nitrite ion concentrations in all the five real ground water samples are reduced to below the permissible limits.

The bio-sorbent developed in this study is successfully applied in waste water treatment technologies because it is inexpensive and most effective adsorbent in controlling the water pollution.

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