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Removal of nitrites from waste waters using adsorbents derived from *Phyllanthus Neruri* plant

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The bio-sorbents prepared from leaves, stems and leaves ashes of *Phyllanthus Neruri* plants have been investigated for their adsorption abilities towards nitrites from polluted waters adopting batch methods of extractions. Physicochemical parameters such as *p*H, sorbent dosage, initial nitrite concentration and time of agitation have been optimized for the maximum extraction of nitrites. The effect of commonly found co-ions on the % of extraction of nitrite has been investigated. Freudlich and 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 the adsorbents. Kinetics of adsorption process is analyzed using pseudo first-order and pseudo-second-order equations and found the good correlation with pseudo second-order model. The methodologies are successfully applied in removing nitrites from water samples collected from polluted lakes.

Keywords: Nitrites, Pollution control, Bio-adsorbents, *Phyllanthus Neruri*

Bio-sorbents are being widely been used in pollution control research and in fact, our research group is thriving on these aspects and found some successful solutions for the removal of various pollutants from waster waters[1-7]. While we are probing various plant materials as the bio-adsorbents in the removal of nitrites from waters, we noticed the affinity between *Phyllanthus Neruri* plant derivates and nitrite ions. The present article is a comprehensive account of our investigations on the extraction of nitrite from polluted waters.

The investigations in removing nitrite ions from waste waters assume importance as nitrite is toxic and causes methemaglobinemia and even cancer and especially in advanced countries half of the cancer deaths are attributed to nitrite ions which react in human or animal stomach to produce cancer causing N-nitroso compounds. Many countries enforced strict legislation to control the nitrite prone cancer and the maximum allowed limits in waters are: 0.5 ppm in EU, I ppm in USA and 0.002 ppm in China[8-19].

The presence of nitrite ions in waste waters are due to the incomplete oxidation of nitrogenous organic matter in waters originating especially from the effluents of industries based on curing meat, fish, vegetables and dairy products. Meat products fermented or poorly stored vegetables and pickles possess enriched levels of nitrite concentration.

Literature survey shows that there are some researches investigating in controlling this potential toxic ion in waters[20-28]. De *et al*.[24] made kinetic studies of the electrochemical treatment of nitrite and nitrate ions on Iridium-modified Carbon Fiber Electrode. Saleem *et al*.[28] studied electrochemical removal of nitrite in simulated aquaculture. Katsuya Abe *et al*.[29] investigated the aerial microalgae Trentepohlia aurea in relation to the removal characteristics of nitrites. Polatides *et al*.[30] 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 use of bio-sorbents in the removal of nitrites is less trodden. Nes, e. Ozturk *et al*.[31] investigated the removal of nitrite from aqueous solution by adsorption using Sepiolite and powdered activated carbon.

The present work is a thorough investigation on the extraction nature of bio-adsorbents derived of *Phyllanthus Neruri* plant towards nitrate ions from waters. The optimum conditions for the maximum removal of nitrate are evaluated adopting batch conditions of extraction by changing the physicochemical parameters such as *p*H, contact time, adsorbent dose, initial concentration of the nitrite ion and effect of interfering ions. The adsorption mechanism is analyzed using Freundlich and Langmuir isotherms and kinetics of adsorption is studied using first-order, pseudo second-order models. The procedures developed are probed for their adoptability using real polluted water samples.

Experimental Section

Chemicals and Solutions

Analytical Reagent grade (Merck) chemicals were used. Suitable concentrations of nitrite solutions were prepared. Stock solution of 500 mg/L was prepared. Sulphanilic acid reagent, α-Napthylamine reagent and Sodium acetate (2M) were prepared as described in Standard methods for the Examination of water and waste water[16].

Adsorbents

Our pilot experiments revealed that the bio-sorbents derived from leaves, stems and ashes of leaves of *Phyllanthus Neruri* have been found to have affinity towards nitrite ions.

Phyllanthus neruri is a wide spread tropical plant commonly found in coastal areas and belonging to the Phyllanthus genus of family Phyllanthaceae and it is found to have many therapeutic values.

Preparation of sorbents

The leaves and stems of *Phyllanthus neruri* were cut, washed with distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: <75 microns and activated at 105°C in an oven and then employed in this study. Further, the leaves of the said plant were burnt to ashes, meshed and used in this work.

Adsorption experiment

The batch methods of extraction procedure were employed[32-34]. Weighed quantities of adsorbents were taken into previously washed 1 L/500 mL stopper bottles containing 500 mL /250L of nitrite solutions of predetermined concentrations. The various initial *p*H values of the suspensions were adjusted with dil. HCl or dil. NaOH solution using *p*H 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 was determined spectrophotometrically[35].

Estimation of nitrites

A measured quantity of the nitrite sample was taken in to a 50 L volumetric flask. To it 1 L 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 L of the α-napthylamine solution and 1 L of 2M-Sodium acetate solution to act as buffer (*p*H 2.0-2.5) were added. The solution was then diluted to 50 mL and mixed well. After 10 min, but not later than 30 min, the Optical Density of the reddish-purple colour 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 unknown samples.

Nitrite ion analysis

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

$$\% \text{ Removal } (\% \text{ R}) = \frac{(\text{Ci}-\text{Ce})}{\text{Ci}} \times 100$$

$$\text{Amount adsorbed } (q_e) = \frac{(\text{Ci}-\text{Ce})}{\text{m}} \text{V}$$

where C_i = initial concentration of the nitrite solution in mg/L

C_e = equilibrium concentration of the nitrite solution in mg/L

m = mass of the adsorbent in grams; V = volume of nitrite test solution in liter

Result and Discussion

Effect of various physicochemical parameters

The adsorption nature of bio-sorbents prepared from leaves and stem powders and ashes of leaves of *Phyllanthus Neruri* towards nitrite ions has been investigated by varying the parameters such as *p*H of the equilibration system, time of agitation, adsorbent dosage and initial concentration of the nitrite ion. The obtained results were plotted and shown in Fig. 1a-d.

The percentage of extraction is found to be *p*H sensitive. With the increasing *p*H, extractability of nitrite decreases for a fixed adsorbent concentration (Fig. 1a). The lingo celluloses' materials have -OH/COOH groups and their dissociation is *p*H dependent. At high *p*H values, these groups dissociates and imparts weak cation exchange ability

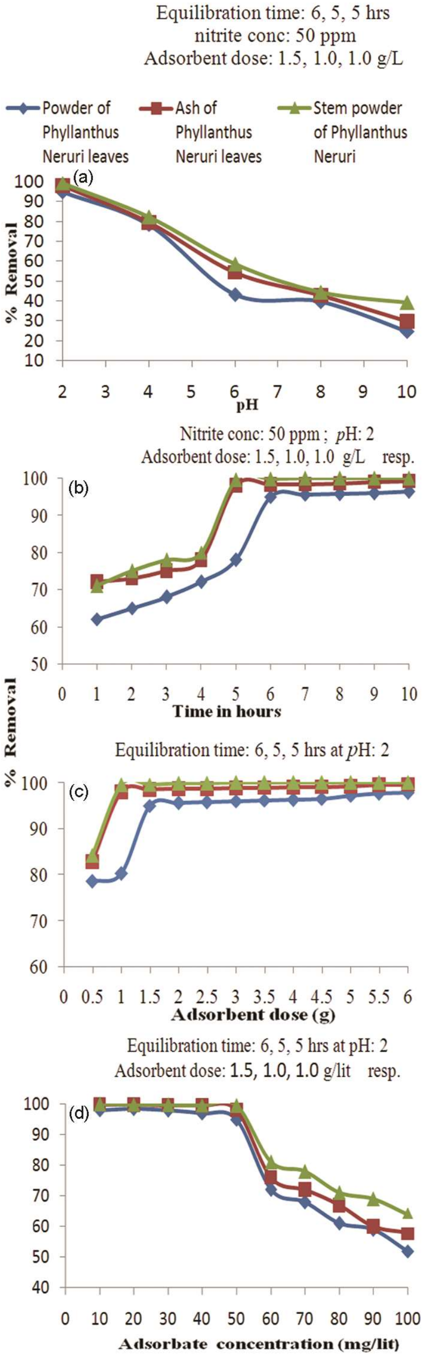

Fig. 1a— Effect of *p*H on % removal of nitrite
Fig. 1b— Effect of Equilibration time on % removal of nitrite
Fig. 1c— Adsorbent concentration vs % removal of nitrite
Fig. 1d—Effect of adsorbent concentration on % removal of nitrite

and at low *p*H 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 *p*H values and hence the high percentage removal. At high *p*H values, cation affinity persists and not anion and hence, nitrite anion show low percentage removal.

At optimum *p*H 2, the maximum extraction of nitrite ions from the simulated waters has been found to be 95.0% with leaves powder (equilibration time: 6 hr and sorbent conc.: 1.5 g/L); 98.0% with leaves ash (equilibration time: 5 hrs and sorbent conc.: 1.0 g/L) and 99.5% (equilibration time: 5 hrs and sorbent conc.: 1.0 g/L) of *Phyllanthus Neruri* plant (Fig.1b).

As contact time increases, initially the percentage removal of nitrite ion increases rapidly and the % of extraction remain constant after certain duration and in other words, an equilibrium state is attained (vide Fig. 1b). This nature of adsorption may be attributed to the fact that initially vacant active sites are available more for the adsorption of nitrites and as the time proceeds, the active sites are progressively used up and a study state is resulted[36,37]. The optimum contract time is found to be 6 hours for leaves powders and 5 hr for the ashes of leaves and stem powder of *Phyllanthus Neruri* plant.

With the increase in adsorbent dosage, % removal of nitrite ion increases and the maximum removal is attained at a certain dosage and then onwards no further removal of nitrite is noted. (vide Fig. 1c). The increase in removal with increase in dosage may be attributed to the increasing availability of number of active sites as well as surface area[38]. After certain dosage, the adsorbed adsorbate ions may either block the access to the internal pores of adsorbent or may cause particles to aggregate (overcrowding of particles) and thereby minimizing the availability of active sites for adsorption[39]. The percentage removal of nitrite is found to be insignificant after a dose of 1.5, 1.0 and 1.0 g/L and hence, these have been fixed as optimum doses of adsorbents: powder of leaves, ash of leaves and stem powder of *Phyllanthus Neruri* respectively.

It is observed that the percentage removal of nitrite gradually decreased with increasing nitrite concentration (Fig. 1d). This might be due to the fact that for a constant adsorbent dosage, total available adsorption sites are limited and hence, insufficient numbers of active sites are available on the adsorbent surface to accommodate nitrite ions at high concentrations of nitrite ions[40,41]. With increase in initial concentration of nitrite ion solution from 10 to 100 mg/L, the percentage removal (% R) decreased from 98.0 to 52.0 % for leaves powders, 99.8 to 58.0 % for leaves ashes and 99.9 to 64.0 % for stems powders of *Phyllanthus Neruri* plant (Fig. 1d).

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, iron, nickel, 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 sorbents were added. Optimum *p*H was adjusted with dil. HCl or dil. NaOH using *p*H 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 1.

Cations, even in tenfold excess, are not interfering with the extraction of nitrite ions at the optimum conditions of extractions as cited in the Table 1. The anions except sulphate, have marginal interference. Sulphate interferes but the interesting point is that the % of extraction of nitrite never comes down 73.0%.

Adsorption Isotherms

The adsorption isotherms are used to describe the adsorbate interaction with adsorbent at equilibrium. Freundlich adsorption isotherm[42] is applied to multilayer adsorption with the heterogeneous surface[43-44] of the adsorbent. Its linearized equation is expressed as:

$$\log(\mathrm{q_e}) = \log \mathrm{k_F} + \frac{1}{\mathrm{n}} \log \mathrm{C_e}$$

Langmuir[45] adsorption isotherm is applied to monolayer adsorption with the homogeneous surface [43-44] of the adsorbent.

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

The essential features of the Langmuir isotherm model can be expressed in terms of a dimensionless constant, commonly known as separation factor, R_L, and it can be represented as:

$$R_L = 1/\ (1+a_L C_i)$$

According to Hall *et al.*[46] the separation factor, R_L indicates the isotherms shape and the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). In these equations, k_F and $1/n$ are the Freundlich constants, C_i and C_e are the initial and equilibrium concentrations of nitrite respectively, 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 plots and values of the Freundlich and Langmuir adsorption isotherm constants together with the correlation coefficients values are presented in Figs 2 and 3 and Table 2 respectively.

The correlation coefficient (R^2) value is used to judge the most fitted model. In the Langmuir adsorption isotherms, the correlation coefficient values are found to be higher (Table 2) and the dimensionless separation factor values are found to be in the range between zero to one (Table 2). These two facts have indicate the favorability of the Langmuir adsorption isotherm than the Freundlich isotherm and confirmed the monolayer coverage of nitrite ion on the surface of adsorbents[47] and also the homogeneous distribution of active sites on the adsorbents since the Langmuir isotherm referred to homogeneous adsorption.

Table 1 — Effect of interfering ions on the Extractability of nitrite with different bio-sorbents derived from *Phyllanthus Neruri* plant

S. No.	Adsor-bents	Maximum extractability at optimum conditions	% of Extraction of nitrite in the presence of tenfold excess of interfering ions at optimum extraction conditions											
			SO_4^{2-}	NO_3^-	Cl^-	PO_4^{2-}	F^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Fe^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}
1	Leaves powder	95.0 %, *p*H: 2, 6 hrs, 1.5 g/L	74.5	85.5	96.5	94.2	94.7	97.5	99.2	98.6	98.9	99.4	99.5	99.8
2	Ash of leaves	98.0%, *p*H:2, 5hrs, 1.0 g/L	75.0	87.4	97.5	96.5	95.1	99.4	100	100	100	100	100	100
3	Stems powder	99.5 %, *p*H:2, 5 hrs, 1.0 g/L	73.0	89.3	95.4	97.2	95.5	97.5	100	100	100	100	100	100

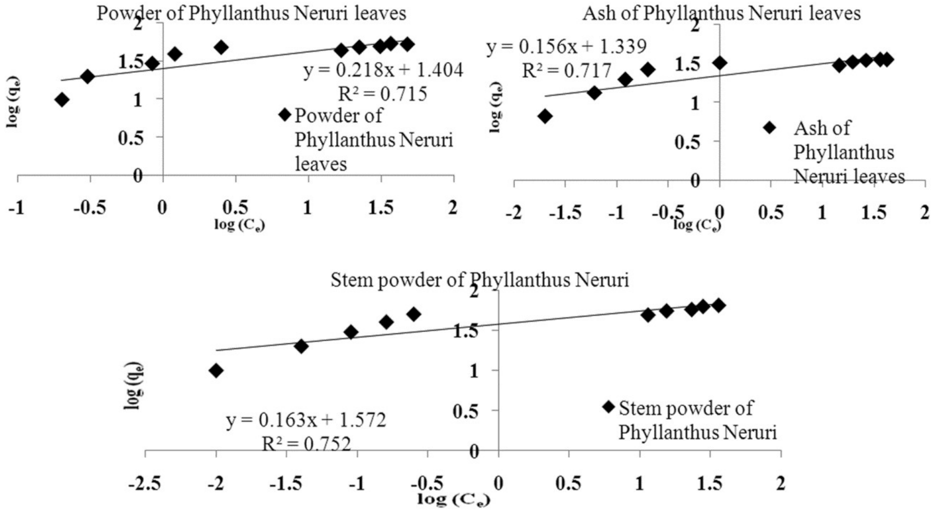

Fig 2 — Freundlich adsorption isotherms

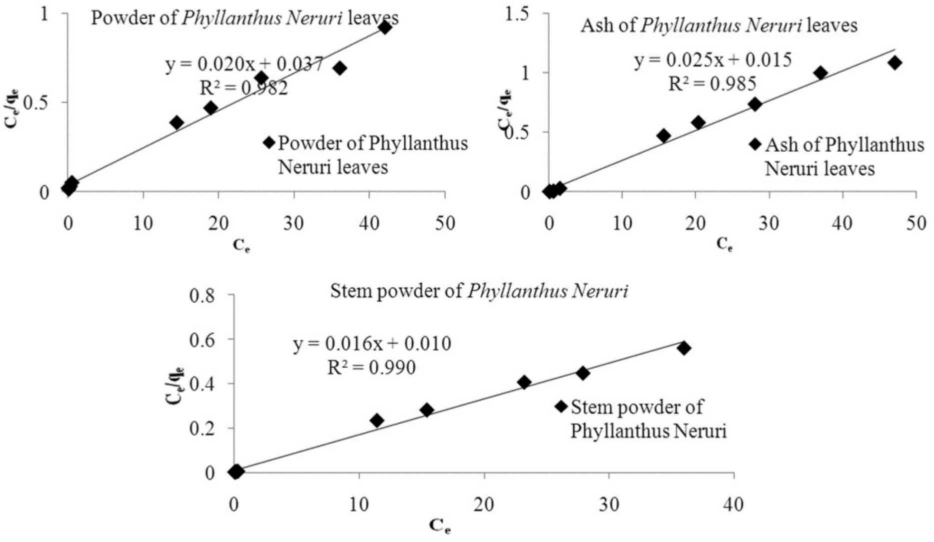

Fig. 3— Langmuir adsorption isotherms

Table 2 — Freundlich and Langmuir constants with the correlation coefficients

Adsorbents	Freundlich isotherm			Langmuir isotherm			
	Slope	Intercept	R^2	Slope	Intercept	R_L	R^2
Powder of *Phyllanthus neruri* leaves	0.2183	1.4041	0.7151	0.0209	0.0378	0.0349	0.9822
Ash of *Phyllanthus neruri* leaves	0.1563	1.3399	0.7178	0.0250	0.0159	0.0126	0.9854
Stem powder of *Phyllanthus neruri*	0.1639	1.5723	0.7528	0.0161	0.0105	0.0124	0.9907

Adsorption kinetics

Kinetic study on adsorption process is significant as it describes the rate of molecular uptake from the adsorbate solution to the adsorbent surface[48]. The pseudo first-order model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo first-order equation of Lagergren[49] is widely used to describe the adsorption of adsorbate from the liquid phase.

The pseudo-first order equation is expressed as log $(q_e\text{-}q_t) = \log(q_e) - \frac{k_1\,t}{2.303}$

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. The pseudo second order rate equation[50-51] is expressed as:

$$\frac{t}{qt} = \frac{1}{k_2 q^2_e} + \frac{1}{q_e}(t)$$

where, q_e and q_t are the amount adsorbed (mg/g) at equilibrium and at time t, respectively and k_1 (min^{-1}) and k_2 (g/mg.min) are the rate constants of the pseudo first-order and pseudo second-order adsorption process.

The plots and values of the pseudo-first-order and pseudo second-order rate constants together with the correlation coefficients values were presented in Fig. 4 & 5 and Table 3 respectively.

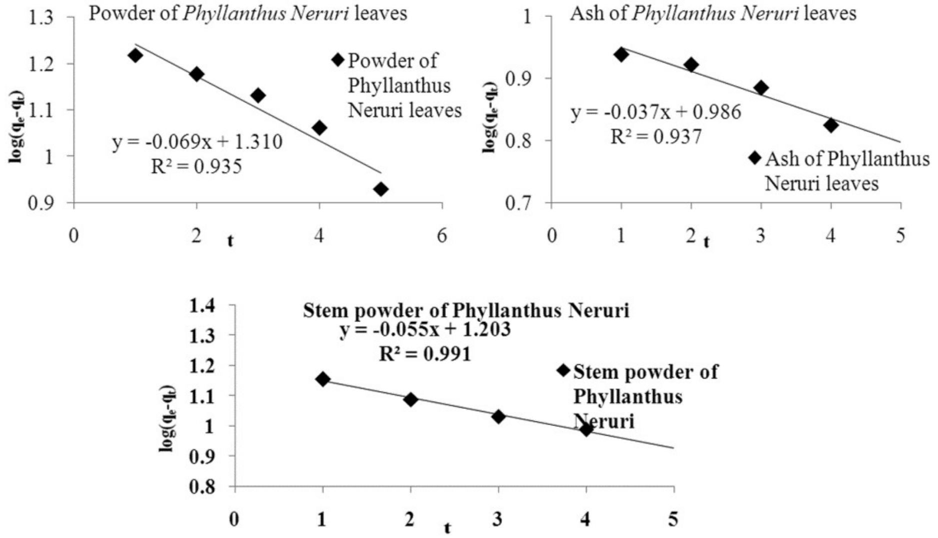

Fig. 4 — Pseudo first-order kinetics

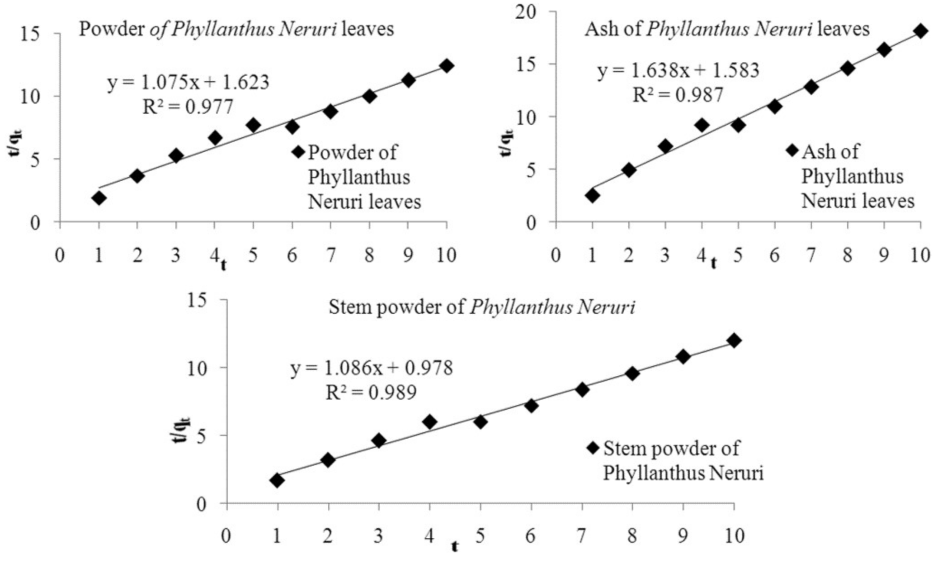

Fig. 5 — Pseudo-second order kinetics

Table 3 — Pseudo first and second-order rate constants with the correlation coefficients

Adsorbents	Pseudo first-order			Pseudo second-order		
	Slope	Intercept	R^2	Slope	Intercept	R^2
Powder of *Phyllanthus neruri* leaves	-0.0691	1.3102	0.9356	1.0751	1.6232	0.9770
Ash of *Phyllanthus neruri* leaves	-0.0378	0.9865	0.9373	1.6387	1.5833	0.9873
Stem powder of *Phyllanthus neruri*	-0.0551	1.2034	0.9911	1.0866	0.9784	0.9895

Table 4 — Percentage of extraction of nitrites from polluted water samples using bio-sorbents developed in this work

S.No.	Adsorbent	Optimum conditions of extraction	Simulated waters (50 ppm)	Polluted water samples				
				Sample 1 \(2.5 ppm)	Sample 2 (5.0 ppm)	Sample 3 (7.5 ppm)	Sample 4 (10.0 ppm)	Sample 5 (12.5 ppm)
1	Leaves powder	*p*H: 2, 6 hr 1.5 g/L	95.0 %	92.0 %	91.5 %	90.5 %	93.5 %	94.0 %
2	Leaves ash	*p*H: 2, 5 hr 1.0 g/L	98.0 %	94.5 %	93.2 %	91.0 %	94.0 %	95.0 %
3	Stem powder	*p*H: 2, 5 hr, 1.0 g/L	99.5 %	97.3 %	94.9 %	93.5 %	96.5 %	96.5 %

If the correlation coefficient (R^2) value is close to unity, more linearity is achieved; this indicates the applicability of the adsorption kinetics. The correlation coefficient, R^2 values for the pseudo

As the correlation coefficient (R^2) value is close to unity, more linearity is achieved and indicated the applicability of the adsorption kinetics[52]. The correlation coefficient, R^2 values for the pseudo second-order adsorption model were found to be close to one than the pseudo first-order model (Table 3). Hence, the pseudo second-order model is best-fit to the experimental data of the present studied adsorbents than the pseudo first-order model.

Application 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 Mandal of Guntur Dist of Andhra Pradesh and the actual concentrations of nitrite present in them were analyzed. Then these samples were subjected to the extraction of nitrites using the bio-sorbents developed in this work at optimum conditions of *p*H, equilibration time and sorbent concentration. The results obtained were presented in the Table 4.

It is found that the sorbents developed in this work are successful in removing more than 90.0% of nitrites from polluted water in these samples of water at optimum extraction conditions as cited in the Table 4.

Conclusion

Powder and ash of *Phyllanthus Neruri* leaves and stem of *Phyllanthus Neruri* have been probed for their sorption properties towards nitrite ions. At low *p*Hs of equilibration, these adsorbents show affinity towards nitrite ions.

Various physicochemical parameters such as *p*H, sorbent dosage, time of agitation and initial concentration of nitrite ions have been optimized for the successful quantitative extraction of nitrite.

We claim 95.0% removal (at equilibration time: 6 hr, *p*H: 2 and adsorbent dosage: 1.5 g/L) with the powder of *Phyllanthus Neruri* leaves; 98.0% removal (at equilibration time: 5 hr, *p*H 2 and adsorbent dosage: 1.0 g/L) with the ash of *Phyllanthus Neruri* leaves and 99.5% removal (at equilibration time: 5 hr, *p*H 2 and adsorbent dosage: 1.5 g/L) with the stem powder of *Phyllanthus Neruri*. The increasing order of the extraction ability is : powder of leaves < ash leaves < stem powder.

Even tenfold excess of common cations and anions except sulphate, normally present in waters have shown only marginal interference with the extraction of nitrites from simulated synthetic waters at the optimum conditions of extraction.

On modeling the adsorption isotherms using Langmuir, and Freundlich methods, it is found that the experimental data is fitted well to Langmuir isotherms indicating monolayer formation on to the surface restraining finite number of identical sorption sites.

Kinetics of adsorption process is fitted well to the pseudo second-order kinetics indicating that adsorption involves valence forces through sharing or exchange of electrons between adsorbate and adsorbent.

The methodologies developed in this work are successfully applied to real polluted water samples.

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