Assimilation of Nitrate Ions onto Surface Modified Biomaterial from Aqueous Environs

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Abstract

Nitrate ions from various sources viz., fertilizers, pesticides, agricultural runoff and sewage wastewaters discharged into water bodies either directly or indirectly may lead to several ailments like methemoglobinemia (Blue baby syndrome) and death of aquatic plants/animals. The present study investigates the utilization of *Eleocarpus tectorius* seed (ETS), a plant waste for the removal of nitrate ions. Excess alkaline nature of ETS is minimized, by treating with 0.1N HCl and characterized using BET/BJH, FTIR and SEM / EDAX analyses. Batch Equilibration studies are performed to examine the effects of particle size / dosage, contact time, initial anion concentrations/ agitation time interval, pH of the medium, temperature and co-anion. The results indicate 99.7% nitrate ions are chelated by treated ETS under optimized conditions of 0.18 mm particle size, 200 mg dosage, 10 mins agitation time, 100 mg/L initial nitrate concentration, pH 5 and room temperature. The generated experimental data are validated with Langmuir, Freundlich and Tempkin Isotherm models wherein both Langmuir and Freundlich plots exhibited a better linear fit with correlation coefficient value nearness to unity supporting monolayer/multilayer sorption. Thermodynamic studies indicate the favourability, exothermicity and spontaneous nature of the system. simulation of pseudo second-order kinetic model is evident from the sorption kinetics studies. The made observations imply that the chosen waste seeds possess excellent anion chelating capability.

Keywords: nitrate, plant waste, batch method, chelation, isotherm.

1. Introduction

Rapid urbanization, agricultural activities and industrialization has lead to the accumulation of vast number of contaminants in the environment. Nitrate ions hold a superlative position in that list and is responsible for contaminating soil, ground and surface waters through varied sources. Wide use of nitrogen rich fertilizers in agriculture is one of the major sources of nitrate pollution. Nitrate ions, being highly soluble in water and does not bind well with the soil particles and thus, easily enter into varied water sources[1]. Excess concentration of nitrate in drinking water is a potential threat to human health especially in adults causing gastric problems due to the formation of nitrosamines in water and may cause methemoglobinemia (blue baby syndrome) which results from the conversion of nitrate to nitrite that combines with hemoglobin to form methemoglobin thereby declining the ability of the blood to carry oxygen. Nitrate, in particular, causes outbreaks of infectious diseases such as cancer of the alimentary canal and cyanosis among children. The maximum contaminant level (MCL) for nitrate in drinking water set by the World Health Organization (WHO) and the US Environmental Protection Agency (USEPA) are 50 and 10 mg/L of NO_3^- respectively[2]. Therefore, it is necessary to remove nitrate from aquatic environment.

Different processes have been reported for the removal of nitrate ions from aqueous solutions and wastewaters viz., biological de-nitrification, chemical reduction, reverse osmosis, electrodialysis, adsorption, ion exchange, coagulation, filtration and precipitation. Where adsorption technique is a promising one due to its economical and simple operation. In addition, most adsorptive materials are regenerable, pose less sludge production, fewer disposal problems, renewable, low cost and abundant availability.

The present study investigates the removal efficiency of *Eleocarpus tectorius* seed onto nitrate ion from aqueous solutions.

2. Materials and Methods

2.1 Collection of Material

Eleocarpus is a tropical evergreen tribal tree of Nilgiris, *Eleocarpus tectorius* (ET) is a wild edible fruit employed for therapeutic purpose.[3] It has been reported further, that various ancient tribes had been using this fruit for the treatment of leprosy, pneumonia, rheumatism, ulcers, piles, and dropsy. The roots containing alkaloids, terpenoids, flavonoids serve the treatment of tuberculosis, headache, arthritis, heart disease, asthma, back pain and diarrhoea but for the seeds thrown as litter.[4] The seeds were collected from Balacola, Ooty, washed with distilled water for impurities removal and sun dried for a period of nearly ten days. The dried material was later pulverized using electrical mixer and sieved to various mesh sizes viz., 85BSS, 72BSS, 52BSS, 36BSS and 22BSS using Scientific Test Molecular Sieves (JAYANT Scientific Instruments Co., Mumbai). The sieved material was treated with 0.1N HCl for 3hours washed, dried and labelled as TETS. Fig 1 shows the picture of *Eleocarpus tectorius* seeds and their subdivision imply the laboratory preparation for 85 BSS mesh size.

2.2 Scientific Classification:

Family : Elaeocarpaceae
Genus : Elaeocarpus
Kingdom : Plantae
Clade : Angisperms, Eudicots, Rosids
Order : Oxalidales

Fig 1 : *Eleocarpus Tectorius* fruit

Fig1a – Raw ETS

Fig1b – Crushed ETS

Fig1c – Treated ETS

2.3 Preparation of Sorbate

A stock solution of 1000 mg/L of nitrate ion was prepared using appropriate dose of KNO_3.[5] A standard of 100 mg/L was prepared from the stock solution and further dilutions were made as working aliquots as per the experimental requirements.

2.4 Batch Equilibration Experiments

The sorption efficiency of TETS in sequestration of nitrate ions is assessed through the influence of operating factors viz., particle sizes (0.18mm-0.71 mm) and dosages (50 mg- 250 mg: 50 mg) of TETS, initial concentrations (50, 100, 150, 200 and 250 mg/L) of nitrate aliquots, agitation time between the sorbate and sorbent species (5 - 30 min: 5 min), pH of the medium (3, 5, 7, 9 and 11), co – anions (PO_4^{3-}, SO_4^{2-}, Cl^- and F^-) and temperature (273K-313K). 50 ml of sorbate solutions of the concentration ranges were pipetted in 250 mL concentrations nitrate ion were taken in 250 ml Erlenmeyer flasks and appropriate doses of TETS with specified sizes were added. The mixtures were agitated in a Rotary Shaker (KEMI) at 140 rpm/ minute at preset time intervals, at modified temperatures. pH values were recorded for the sorbate species before and after the sorption process using ELICO pH meter. The initial and final absorbance values corresponding to nitrate ions were analysed using UV - Vis spectrophotometer (Lab India 3000) by Azo dye complexation method (λ_{max} = 550nm).

The percentage of anion was calculated using the following equation,

% Adsorption = $(C_i - C_e)/ C_i * 100$

The amounts of anion (**q**) in the sorption system was calculated as per mass balance equation,

$q = v (C_i - C_e) / w$

where, v is the volume of the sorbate (mL), w is the mass of the adsorbent (g), C_i and C_e are initial and equilibrium nitrate concentrations (mg/L) respectively.

3.Experimental Verification Studies

Fourier transform infrared (FT-IR) spectra were recorded (IR affinity 1- Shimadzu) spectrophotometer for both unloaded and nitrate laden TETS in order to assess the involved functional groups during adsorption. The sorbent morphology was analysed using Scanning Electron Microscope (SEM – ZIESS). Surface areas and pore characteristics of the prepared adsorbents were determined using the Bruner-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) plots respectively, employing nitrogen adsorption on an Accelerated Surface Area and Porosimetry System. The mathematical isotherm models developed by Langmuir, Freundlich and Tempkin and sorption kinetics viz., pseudo- first order and pseudo-second order. were applied to the experimental results and the nature of the system was studied. Standard free energy, enthalpy and entropy changes were calculated from the thermodynamic parameters to determine the possibility and feasibility of the sorption reactions.

4. Results and Discussion

Table 1 implies that TETS exhibits neutral pH and lesser moisture content value indicative of its stable nature with seldom storage problem[3]. Ash content values the presence of scrimpy inorganic matter with abundant carbon content. Specific gravity value < 2.0 supports the lower surface tension, thereby the sorption process is favoured. Bulk density value less than unity reveal the presence of fine particles with higher pore volume. The porosity value (63.7 Å) lying between (20 Å < d< 500 Å) specifies that TETP is mesoporous in nature.

Table 1 Physiochemical Parameters

Properties	TETS

pH	7.17
Moisture Content (%)	1.64
Ash Content (%)	3.12
Specific Gravity	1.46
Bulk Density (g/cm^3)	0.59
Porosity	63.7

4.1 BET and BJH Analyses

Figures 2a, 2b, 2c confine to the surface and pore nature of TETS. The adsorption performance is highly dependent on the internal pore structure. The linearity of BET plot indicates prominent surface area and pore size distribution in favour of mesoporous nature of TETP. Specific pore volume was determined based on the pattern of lines as evident from BJH analysis. A typical N_2 sorption isotherm with adsorption and desorption curves, that is the hysteresis loop observed between the lower adsorption and upper desorption curves in fig 2c support the existence of mesoporic nature[6]. The surface area and mean pore diameter calculated from BET/ BJH plots are 29.363 m^2/ g and 1.485 nm respectively.

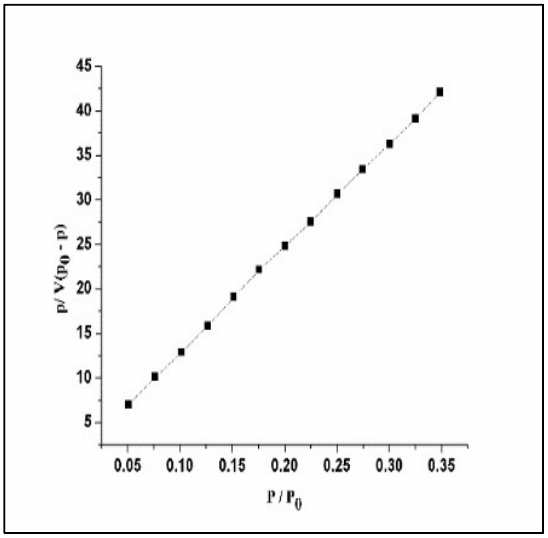

Fig: 2a BET Plot

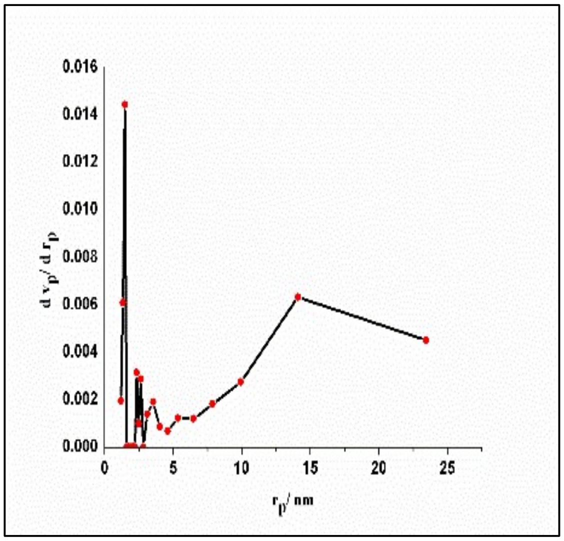

Fig: 2b BJH Plot

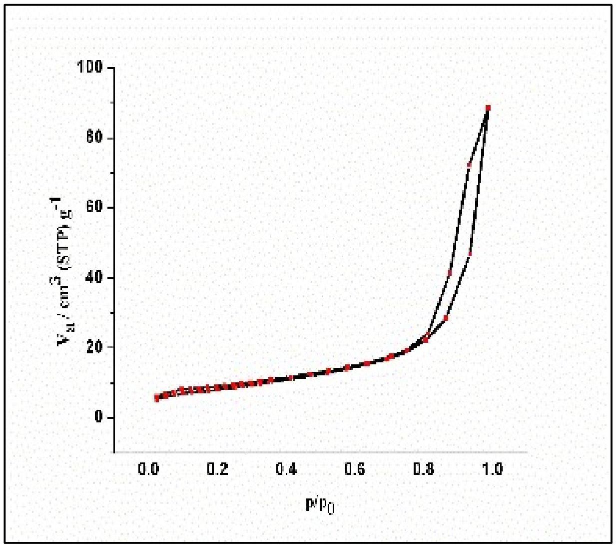

Fig 2c Adsorption/Desorption Plot

4.2 FTIR Spectral Studies

FTIR spectra recorded corresponding to TETS and its loaded sample (figs 3a&b) show a shift in the wave numbers of prominent peaks.[7] The adsorption band at 1522.87 cm^{-1} and 1041.81 cm^{-1} refers to carbonyl group and R-CH, R-OH vibrations[6]. The adsorption by TETS might be attributed mainly to their surface, the band at higher frequency of 3735.31 cm^{-1} indicates the occlusion of water in solid surface. This is a sound proof that nitrate ions were sorbed by electrostatic attraction.

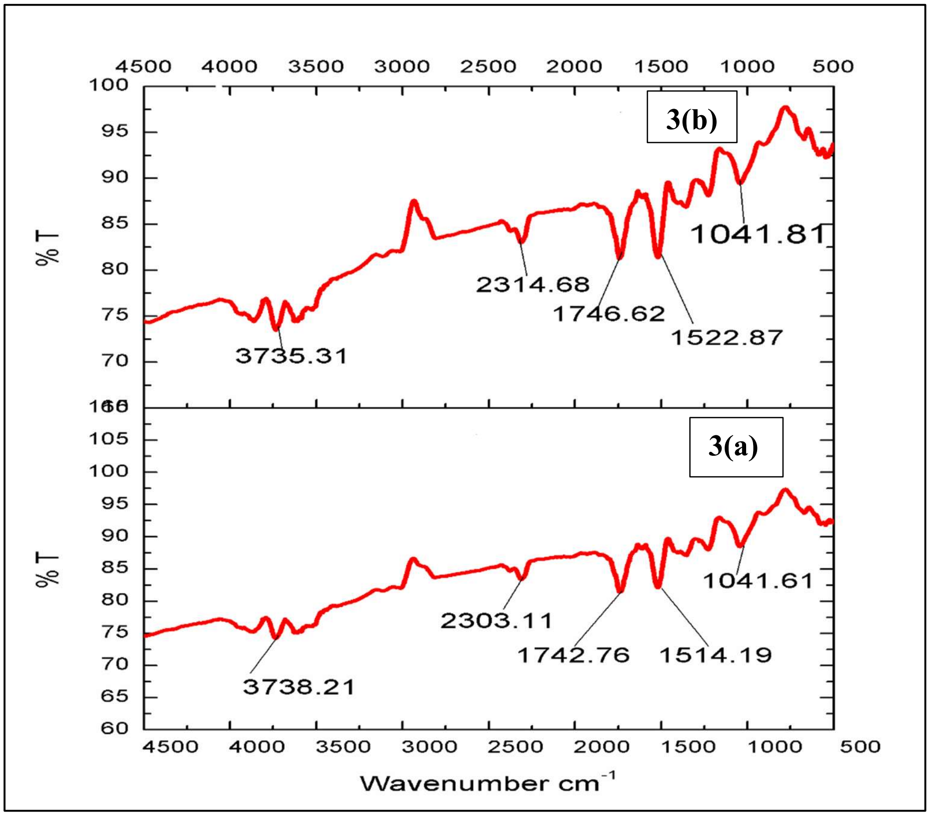

Fig: 3(a) Unloaded TETS, 3(b) Loaded TETS

4.3 SEM/EDAX Analysis

SEM images of TETS and nitrate laden TETS are represented in (Figs 4a & b). the morphological aspects of unloaded image shows opening up of pores on the sample surface implying a ruggedness against its loaded precursor, this confirms that the chemical treatment expanded the pores of the solid surface.[8] After anion sorption pores were blocked indicates the smooth morphology. Further confirmed by new spectral peak present at1.51 kev (fig 5b) in EDAX spectrum.

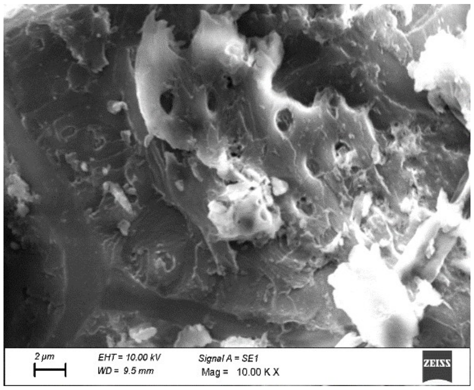

Fig 4(a) - Unloaded TETS

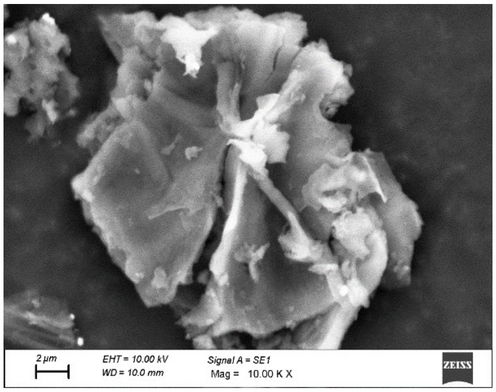

Fig 4(a) - Loaded TETS

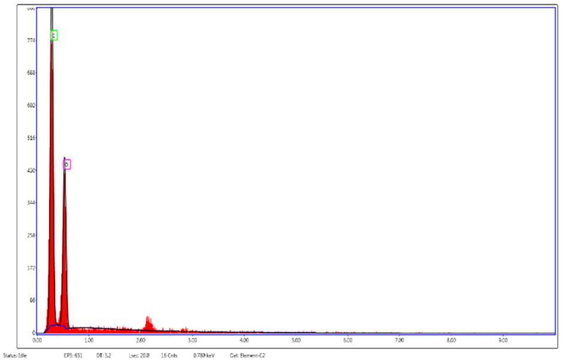

Fig 5(a) - Unloaded TETS

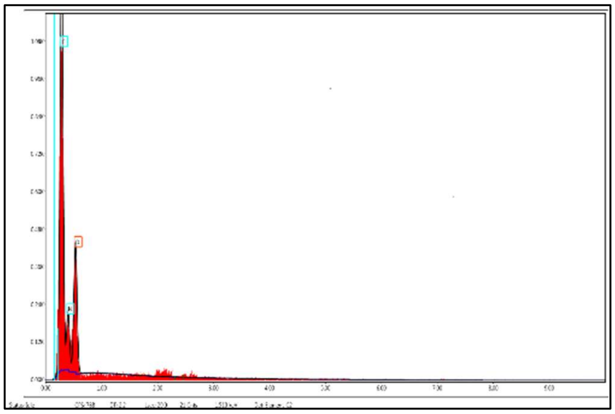

Fig 5(b) - loaded TETS

4.4 Effect of Particle Size

The sorbent particle size plays a crucial role in the biosorption phenomenon of sorbate chelation. Amongst the varied particle sizes experimentally verified, 0.18mm exhibited maximum nitrate ion removal of 99.7% as obvious from fig 6. Smaller particle size offers a larger surface area possessing the tendency to equilibrate in a shorter time. Thence, 0.18mm particle size is fixed as optimum size for the forthcoming experiments

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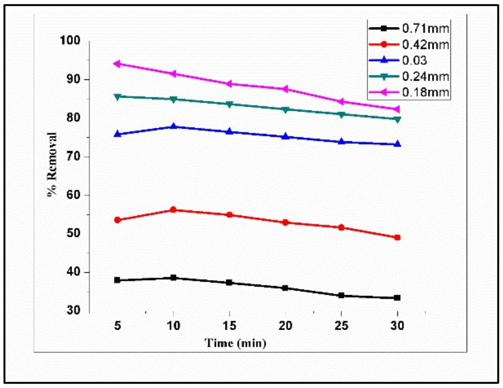

Fig 6 – particle size

4.5 Effect of Dosage

Fig 7 depicts the influence of varying doses of TETS on the adsorption process. 200mg TETP was optimum for maximum nitrate sorption beyond which the sorption rate diminished.

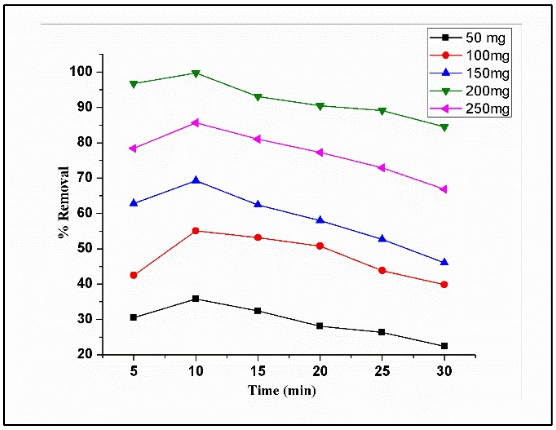

Fig 7 - Dosage

4.6 Effect of Initial Concentration/Contact Time

The influences of initial anion concentration (50 – 200 mg/L: 50 mg/L) and contact time (5 - 30 mins: 5 mins) for NO_3^- – TETS system are shown in fig 8. Attainment of equilibrium had occurred at a contact time of 10 minutes beyond which the system reached a saturation point.[9] A gradual gradation in nitrate percentage removal had occurred upto 100 mg/L of initial nitrate concentration after that decline in the removal is obvious from the graph. The lowering of anion uptake, shall be because of excess anions left unabsorbed in the solution. Thenceforth, 100 mg/L and 10 minutes were fixed as the optimum concentration and agitation time for the system.

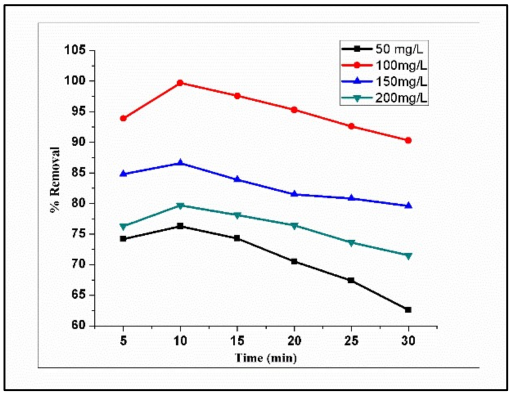

Fig 8 - Initial anion concentration/Contact Time

4.7 Effect of pH

pH, an important parameter shall change or control the solubility/ degree of rapid ionization of anions and concentration of counter ions being adsorbed. The sorption trend with respect to different pH environments reveal an inverted parabolic like curv, where ultimate nitrate removal (99.7%) had occurred at pH 5 (fig 9) beyond which at alkaline pH, the agitation registered a decline in the sorption process which shall be due to competence of OH^- with NO_3^- ions is getting preferentially sorbed on TETP surface.[10]

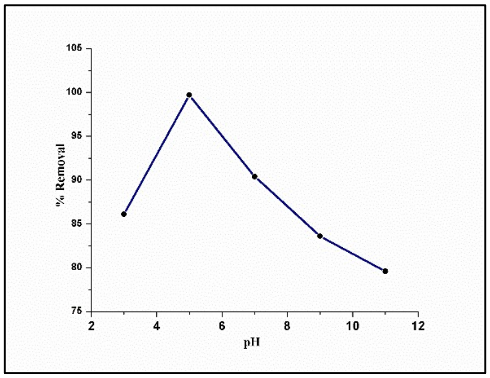

Fig 9 - pH

4.8 Effect of Coexisting Anions

The extrability of nitrate ions in presence of common anions presents in water bodies namely phosphate, sulfate, chloride and fluoride is illustrated in fig 10, which show nitrate ion removal efficiency drastically fell in presence of phosphate ion and moderately decreased with sulfate ion and marginally decreased in presence of chloride and fluoride ion. The adsorption occurred through the electrostatic attaction between positive surface charges on the sorbent and negative charges on the sorbate by outer sphere surface complexation[11]. phosphate has three valence charges and it has a tendency to adsorb stronger than sulfate which has two valence charge and choride and fluoride has one valence charge.[12]

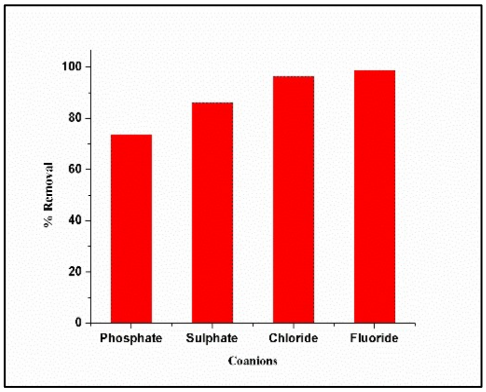

Fig 10 - Coanions

4.9 Adsorption Isotherms

Adsorption isotherms explain the distribution of the adsorbate species between solid and liquid phases of the system and provide information regarding adsorption mechanism.[13]

Langmuir Isotherm

Langmuir graph (fig11) plotted as the ratio of equilibrium concentration and sorption capacity against equilibrium concentration registered a straight line and the derived constants q_m and b are listed in table 2.

Freundlich Isotherm

Freundlich plot (fig 12) arrived from logarithimic values of adsorption capacities and equlibrium concentrations of nitrate ions exhibited a linear fit, from whose slope and intercept the freundlich constants of K_f and 1/n were deduced.

Tempkin Isotherm

Tempkin isotherm is focussed on the assumption that the free energy of sorption is a function of the surface coverage. Tempkin constants A_T and B_T (table 2) were calculated from the intercept and slope of an approximate linear plot (qe vs ln Ce) illustrated in fig 13.

Correlation coefficient (R^2) pertaining to the studied isotherms suggest that system follows both monolayer/multilayer sorption. This specify ion exchange explains the sorption mechanism.

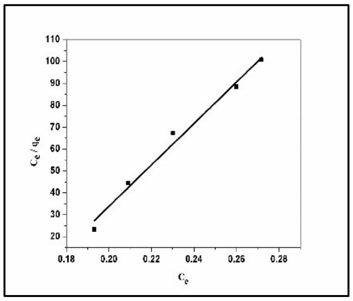

Fig 11- Langmuir plot

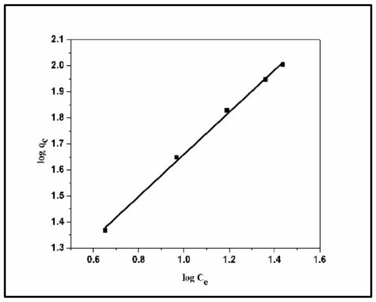

Fig 12 - Freundlich plot

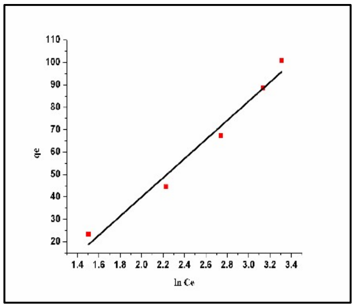

Fig 13 - Tempkin plot

Table 2: Adsorption Isotherm

Langmuir Isotherm		Freundlich Isotherm		Tempkin Isotherm	
q_m (mg/g)	285.71	K_F (mg/g)	7.10	A_T (L/g)	59.058
b (L/g)	50.51	1/n	1.23	B_T	0.46
R^2	0.9981	R^2	0.9974	R^2	0.9775

4.10 Adsorption Kinetics

The kinetic studies predict the progress of adsorption. However, the determination of the adsorption mechanism is also important for design purposes. In order to investigate the adsorption kinetics of the nitrate on TETS, pseudo first – order and pseudo second order kinetics were used.

Pseudo first/ second order kinetics

The data corresponding to pseudo-first-order / second – order kinetic models are represented in table 4 and their relative linear plots are shown in Figs 14 and 15. The first order rate constants (qe_1, K_1); second order rate constants (qe_2, K_2), along with corresponding R^2 values determined from the slopes and intercepts of derived plots are listed in Table 3, reveals linear correlation coefficient value (R^2) is relatively higher for pseudo second order model. This facilitates the better description of the adsorption system by pseudo second order kinetic model.

Table 3: Adsorption kinetics

Pseudo-first-order kinetics		Pseudo-second-order kinetics	
qe cal. (mg/g)	0.23	qe cal. (mg/g)	26.24
$k_1\times10^{-2}$ (min $^{-1}$)	322.4	$k_2\times10^{-3}$ (g/ mg min)	1.67
R^2	0.9666	R^2	0.9942

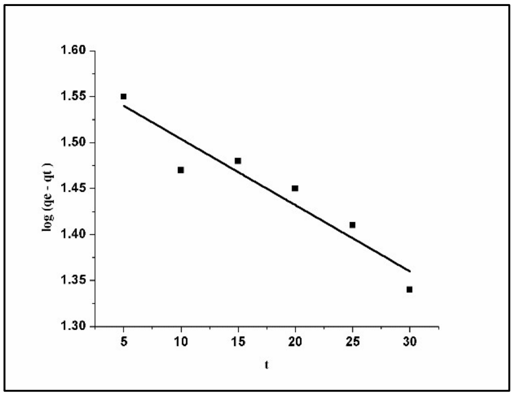

Fig 14 – Pseudo first order plot

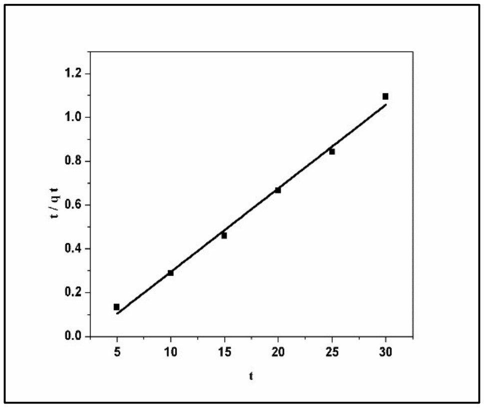

Fig 15 – Pseudo second order plot

4.11 Thermodynamic parameters

The thermodynsmic constants free energy change (ΔG^0), by the following equation $\Delta G = -RT \ln Kc$[15]. The enthalpy (ΔH^0) and entropy (ΔS^0) were calculated from slope and intercept values of Vant Hoff's plot respectively.

The negative values of ΔG^0 (table 4) indicate the spontaneous nature of the adsorption. The negative value of (ΔH^0) suggest that the sorption process is exothermic nature and the positive value of (ΔS^0) indicates that there is the randomness in the solid/solution interface.

Table 4: Adsorption Dynamics

Temperature (K)	**$\Delta G°X10^{-3}$ (kJ/mol)**	**$\Delta H°$ (kJ/mol)**	**$\Delta S°$ (J/mol K)**
273	-0.18	-10.82	45.91
283	-0.20		
293	-0.25		
303	-0.29		
313	-0.37		

5. Conclusion

Eleocarpus tectorius fruit seeds discarded as litter were collected from Balacola, Ooty, dried, crushed and subjected to equilibration studies to evaluate its trapping ability of nitrate ions. The batch studies indicated nearly 100% removal on NO_3^- by TETS at optimized condition of 0.18 mm sorbent's particle size, 100 mg/L initial metal concentration, 200 mg sorbent dosage, 10 min equilibration time and pH 5 at room temperature. Physio-chemical parameters, FT-IR, SEM/ EDAX analyses of unloaded and loaded TETS registered the whole mass adsorption process. The sorption data fitted well with Langmuir and Freundlich plots favouring both monolayer/multilayer adsorption process. The sorption kinetic studies followed Pseudo second order mechanism. Thermodynamic calculations indicated the feasibility, exothermicity and spontaneity of the adsorption process. Thus, it is concluded that this inexpensive material is promising adsorbent for trapping anion from laboratory aqueous solutions. The future scope of this work lies in the initiation of scaling up the adsorption process to industrial leachates.

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