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Benign Graphite-Chitosan blended bio-composite for sorption of toxic nitrate from Water

Dr. Rashmi Joshi[1] , Dr. Rajendra S. Dongre[2],
[1]Associate Professor, Department of General Engineering ,Tulsiramji Gaikwad College of Engineering, Mohgaon,Wardha Road, Nagpur- 441108, (M.S.) India.
[2] Reader,Department of Chemistry, RTM Nagpur University, Nagpur-440033, (M.S.) India.

Abstract:*Assorted nitrogen/phosphorous fertilizer, pesticide and nutrient usage is intensified for crop developments in agricultures in past few decades. Unused nitrate get percolated from sandy/textured soil during rains. Nitrate poisoning imparts methemo-globinemia/blue-baby syndrome besides eutrophication as detrimental to human and ecosystem both. Nitrate contamination is mitigated by water de-nitrification being achieved via various treatments viz; ion exchange resins, reverse osmosis and distillation. Ion exchange operates at household level, softener filters calcium/magnesium laden water passed through resins which exchanges chloride for nitrate. Regeneration of resin is costly issue, so ion exchange is not preferred. Reverse osmosis RO is helpful, but own some disadvantages viz; expensive, high energy inputs, inefficient, squander more water and operates at low pressure. Distillation being slow and seek frequent cleaning for accumulated matter removals is unsuitable for large scale water treatments. Consequently, adsorption onto fabricated natural and synthetic adsorbents is most viable and opted for nitrate removal from water.*

This research derived chitosan based bio-composite by doping graphite and used for nitrate removal from water in batch modes. Lower concentrations of nitrates removed faster; while for higher nitrate level gets removed slowly. Highest 90 % removal efficiency is observed for 5-ppm nitrate sample while 10,15,20,25,and 50 ppm nitrate sample showed 88 %, 79%, 71%, 66%, 60% respective nitrate removal capacity. Langmuir and Freundlich isotherms are examined for experimental data and Langmuir fits best. Graphite doped chitosan bio-composite adsorbent appears benign over commercial adsorbents in terms of cost and efficiency. Used adsorbent gets regenerated by treatment with 0.1 N NaOH. Residual nitrate from the effluent/samples after sorption were analyzed by ion chromatogram at fix intervals.

Keywords*: Nitrate, Chitosan, fertilizer, graphite, bio-composite, de-nitrification, water*

I. Introduction

Various nutrients, fertilizers and pesticides are frequently employed for the growth of crop/plants in farming [1]. Nitrates, sulphates and phosphate are the vital for crops/grains development, thus large of synthetic feeds gets consumed in agricultural soils. Most of these used chemicals remain unused and subsequently percolated with rainwater and graves eutrophication: a global environmental problem [1-2]. Eutrophication causes slow-aging of water due to over loaded nutrients, fertilizers and pesticides which boosts extreme growth of algae, after algae die/decompose highly accumulated organic matters deplete water-oxygen and ensuing death of aquatic species, besides endanger to man [2].

Diverse chemical compounds including nitrate and phosphorous contaminate soils and affects worldwide people since 3% terrestrial ecosystem land bears leaching around 30 kg/ha year [3]. Nutrient level above 0.03 ppm drainage through agricultural fields can impose harmful effects and gets serious impacts on surrounding environments [4]. Nitrate contaminations in water also occur via municipal, domestic and industrial wastes due to their untreated wastewaters. US EPA recommended criteria permits nitrate/nitrites 10 ppm level (including total nitrogen contents) in potable water [5-6]. Since excessive nitrate/nitrite in water causes assorted health issues like digestive, respiratory troubles and methemoglobinemiae illness (digestive system ingestion converts oxyhemoglobin to metheglobin and not carry oxygen, so tissues are oxygen deprived so gives blue coloration). Nitrate binds oxygen in red blood cell and depletes which motive suffocates to bluish skin color, around eye/mouth [1-3].

Surplus amount of nitrate/poisoning induce breath shortening, fast heartbeat, recurrent urination, body collapse, coma and rarely death results besides stomach cancer phenomenon [7]. Nitrate is highly stable and more soluble in aqueous conditions besides less precipitative thus, complicated to remove via traditional water treatment options [8]. Nitrate removal/mitigation is achieved through certain known physicochemical and biochemical treatment techniques namely, ion exchange [6], bio-denitrification [7], reverse osmosis/RO [8], electrochemical reduction/ED [9], catalytic reduction [10] and adsorption [11,13]. Electrodialysis reversal/EDR technique performs demineralization via ionic transfer onto ion-selective membranes using direct electric field is high costly and less efficient. Nevertheless these methodologies possess few shortcomings like ion exchange technique is perfect, instead costly ions regeneration and waste brine disposal are critical issues. Biologically treatments techniques require adding carbonecious matter and consequently generate huge biomass waste which creates disposal issues. Electrochemical reduction needs specially electrodes which get inactivated frequently. Nitrite/nitrite is hazardous thus its catalytic reduction via greener technology path is difficult.

Adsorption is largely fascinated/preferred water treatments via sorption by virtue of especial features viz; plain operation, design simplicity and more economic if low-cost adsorbents/bio-materials are used [14]. Consequently, many adsorbents are employed including; carboneous materials, agricultural wastes, ion exchangers, biomaterials/bio-polymers and synthetic adsorbents. Therefore adsorption remains the ultimate reasonably preferred option being economic, facile operation, less waste and design applied for nitrate removal than above mentioned techniques [9-15]. However, adsorption needs to fabricate lofty capacity adsorbent materials owing easy operation and more efficient besides inexpensive. Hence, bio-materials viz; chitin, chitosan and few agricultural waste are vulnerable sources to derive effective adsorbents. Chitosan own certain intrinsic constraints such as small/ particle size, low crystanality, low desorptivity puts hinderance in practical utility of raw form. Thus techniques like surface protonation [16-17], metal doping/immersion [18] and surface modification/grafting/impregnation are done in chitosan skeleton to enhance its desired adsorption features towards specific pollutant removal. Being bio-polymer chitosan caters all such demands of excellent candidate material to be used for adsorption purpose [19]. Chitosan own multi-faceting proactive functionalities like amino, hydroxyl and carboxyl as vital for the adsorption/removal of pollutants [19-21]. Further chitosan possess certain innate notable physico-chemical features namely: chemical stability, high reactivity, and highly chelative selectivity toward many aquatic pollutants [16-23].

However, adsorption capacities of certain adsorbent materials are very small, thus it needs to explore more effective bio-composites that own elevated adsorption capacity. Activated carbon is also utilized as adsorbent in traditional water treatment technologies, nevertheless, it exhibits less removal efficiency and retain nitrate contaminant during adsorption which ultimately depletes overall sorption at increasing levels of nitrates in inlet water sample. Such situation gets minimized via post-treatment operation that boosts extra maintenance. Hence, it needs to seek viability of certain naturally abundant biomaterial based adsorbents including chitin/chitosan (sea food waste) gets indispensible. Thus, this research is based/fabricated multiple adsorptive sites on chitosan derived bio-adsorbents to be used for effective bio-sorption of nitrate from water. Certain shortcomings of chitosan like less crystanality, poor stability and low mechanical strength solubility pattern only soluble below pH=5, [19-21] could not prefer crude chitosan as a suitable adsorbent in treatment processes [14,19-21]. Thus, it needs to rectify such limitations via tunable/tangible skeletal modifications and/or synergistic grafting so as to develop composite/matrix adsorbents. Chitosan skeleton gets appropriately modified through such impregnation/conversion composite. Several physic-chemical processing are carried out onto chitosan framework so that nitrate anion gets adsorbed in quaternary ammonium groups of resultant composite [14, 19]. This research is focus on doping graphite into chitosan skeleton as the cross-linker to yield a novel chitosan-graphite layer intervene hybrid composite owing enhanced adsorption capacity.

II. Experimental

2.1. Materials and Reagent Preparations: Potassium nitrate (KNO_3) was purchased from Aldrich Chemicals, as directly used without any purification for preparation of nitrate sample solutions and sample diluted as needed.

2.2. Analytical methods: The residual concentration of nitrate anions in solution was determined by colorimetric method on UV-VIS SP 2000 spectrophotometer. All the pH was measured by pH-meter and liquid characterization was done in pH measurement.

2.3. Preparation scheme for adsorbent: (20% graphite doped chitosan bio-composite): Raw chitosan cross-linked flakes were dissolved in 5% aqueous acetic acid solution to be transformed into hydrogels. 2-3 % raw chitosan flakes were dispersed in 9:1 ratio of water: acetic acid solution at such moderate acidic conditions/pH found to induce inversion collision that controls hydrophilic and phobic interaction and persuade spontaneous entangling of chitosan cross linked network. This phenomenon pursued coagulation to yield self folded/standing microsphere hydrogel if brought in contact with alkali solution [13-21]. Subsequently these gel forms viscous droplets/bids which was further impregnated/grafted with graphite doping to yield biocomposite depicted in **Figure-1 (i&ii)**. Chitosan's hydrogel drying can cause vivid shrinkage may drop porosity and own continuous pore size range from mesoporous to macroporous with reasonably fair specific surface area attributed to space zones of contacts between chitosan fibrils via amine group impregnation by graphite [13-17].

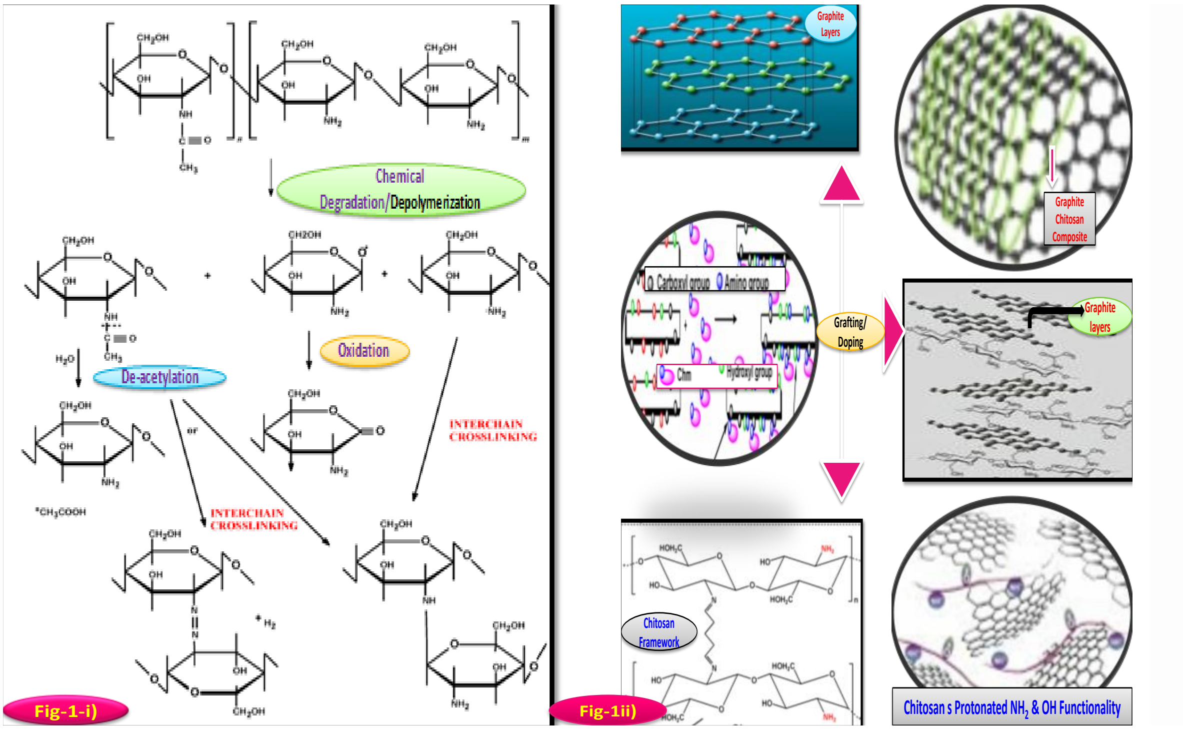

Fig-1: Preparation scheme i) chitosan treatment ii) 20% graphite doped chiotsan bio-composite (5 mm).

2.4. Adsorbent Characterization

i). Elementary Analysis: Elementary analysis viz; C/H/N/S, moisture, surface parameters of adsorbents is depicted in **Table-1.** %Ash obtained via ignition at 800^{0}C and calculated by **Eq^{n} (1).** Gravimetric analysis was used to calculate % moisture content while water mass/weight difference of wet-dried sample calculation was done by using following **Eq^{n} (2):**

% Ash= [Weight of residue (g)/Sample weight (g)] x1 **-------------- Eq^{n} (1)**

% Moisture Content= [Wet weight (g) – Dry Weight (g)]/Wet weight(g)x10 **----------Eq^{n}(2)**

Table 1: Characteristics of chitosan, graphite and graphite doped bio-composite

Parameters	**Doped Bio-composite**	**Raw Chitosan**	**Raw Graphite**
Appearance	Whitish	Slightly Yellowish	Iron-black;luster
Solubility	Insoluble in solvents	2% w/v in 5% acetic acid	hot chlorosulfuric acid
Ash Content	4.0%	2.10%	< 1.0%
Carbon content %	59.4%	42.6 %	> 94 %
Hydrogen content %	3.9%	7.7%	4 %
Nitrogen content %	3.3%	7.9%	Nil
Sulphur content %	0.16%	0.16%	Nil
Oxygen content %	33.33%	33.33%	0.001%
Moisture/H_2O content %	1.0%	2.9%	Nil
Dry stuff content %	Hydrogel– 5.3 %	Flake – 88%	99%
Volatile material content	55%	55%	Nil
Particle size	176µm – 246 µm	75-90 mm	50-75µm
Surface area (m^2/g) BET	3.9 m^2/g	12.9 m^2/g	8-12 m^2/g
Total pore volume cm^3/g	0.002	0.024	0.1-0.3 P/P0
Mean Pore Diameter nm	28.1	10.4	---

ii) Batch adsorption studies: Nitrate elution tests were performed in distilled water over 240 minutes of time span for adsorption experiments. The parameters like pH, conductivity and residual nitrate concentration were measured after 240 minutes span. The analysis was conducted in duplicate under uncontrolled optimized pH for accuracy in batch experimental modes in total sample volume taken 50mL for all batch tests for given nitrate samples solutions owing concentrations 5, 10, 15, 20, 25 and 50 ppm. Graphite doped chitosan bio-composite was taken 1 g/L in 50 mL nitrate solution taken in 100 ml Erlenmeyer flask with different concentrations and kept on mechanical shaker at 200 rpm and allowed to reach equilibrium. Initial nitrate concentration of 5 to 50 ppm was used in this batch mode experiment studies. After every adsorption resultant samples were filtered via Whatman-filter paper and residual nitrate concentrations was determined with average values.

2.5. Adsorption Kinetics: The dynamic adsorption analysis was done and kinetic rates of nitrate adsorption were measured in terms of time in an agitated reactor with a water jacket with maintained adsorption NTP. The % nitrate and corresponding adsorption capacities removal was calculated using following **Eq^{n}** 3, **Eq^{n} 4** and **Eq^{n} 5** respectively.

$$\%\ \textbf{removal} = \frac{C_i - C_f}{C_i} \times 100 \text{---------} (3)$$

$$q_e = \frac{C_i - C_f}{m} \times V \quad \text{-----------} \quad (4)$$

$$q_t = \frac{C_i - C_t}{m} \times V \quad \text{------------------------} (5)$$

where q_e, q_t are nitrate amount as adsorb at equilibrium, and at time t respectively in (mg/g);
C_i and C_f were initial and final nitrate concentration in (mg/L).
C_t = residual adsorbate concentration at time t in (mg/L);
V = volume of solution (L) i.e., is volume of nitrate solutions,
m = mass of adsorbent (g/L).

2.6. Adsorption Isotherms: Langmuir isotherm considers the monolayer coverage of the adsorbate/nitrate over a homogenous surface of adsorbent and at equilibrium adsorption saturation state is achieved where more adsorption/desorption cannot happen [20-21]. While Freundlich is an empirical exponential in nature which considers increase in adsorbate concentration too enhances/more loading input of adsorbate amount onto surface of adsorbent [19-22]. Theoretically, an infinite quantity of adsorption may occur under this situation. Freundlich constants K_f and heterogeneity factor n which are determined from the linear form of the equation and a graph of $\ln q_e$ against $\ln C_e$.nqe which can describe heterogeneous systems. K_f relates bonding energy as defines corresponding adsorption/distribution coefficient and represents quantity of adsorbate adsorbed onto adsorbent for a unit equilibrium concentration. Slope 1/n value range from 0-1 which measures adsorption intensity/surface heterogeneity and it is more heterogeneous if value gets closer to zero. All such correlative adsorption results as drawn from adsorption isotherm can help to percept entire nitrate adsorption more theoretically. Langmuir isotherm is linear and quite applicable in case of monolayer adsorption happens via homogeneous way onto bio-composite surface layers. Following adsorption isotherm **Eq^{n}-6** and **Eq^{n}-7** correlated experimental results [11].

Linear Langmuir Isotherm Equation: Qe= Qmaxb Ce1+bCe ------------- (6)

K directly measures the intensity of adsorption, and q_m constant relates the surface area engaged by a monolayer of adsorbate/nitrate overall it shows adsorption capacity. Plot of C_e/q_e versus C_e, helps to determine q_m and K values from its slope and intercept.

Freundlich Isotherm Equation: Qe=KCe1/n ------------------------------ (7)

Ce= equilibrium concentration (ppm) of nitrate in aqueous solution,
Q_{max} = maximum adsorption capacity (mg/g),
b = Langmuir constant relates binding sites affinity (L/mg),
K= Freundlich constant relates adsorption capacity (L/g) and
n = Adsorption intensity/heterogeneity factor.

2.7. Kinetic isotherms: Amount of nitrate adsorbed per unit mass of bio-composite at NTP was calculated and concentration in equilibrium yield from corresponding isotherm (vitally determines sorption capacity). Rate constants and sorption capacity for nitrate adsorption gets influenced by initial sample quantity, regardless of nitrate concentration, adsorbent showed highest sorption capacity for lower concentration of nitrate samples. Linear Langmuir adsorption isotherm is acceptable since adsorption found homogeneous with maximum adsorption capacity 37.2 mg/g at NTP. All the experimental data were studied for Langmuir and Freundlich isotherm models. Kinetic parameters of nitrate adsorption are determined from pseudo-1st order and pseudo 2nd order models as shown in **Table**-2.

Table-2: Kinetic of nitrate adsorption from pseudo-1st and 2nd order model

Adsorbate	**Concentration**	**Pseudo-first order model (non-linear form)**			**Pseudo-second order model (non-linear form)**			**Exp. Data**
		K_1	**$Q_{e,cal}$**	**R^2**	**K_2**	**$Q_{e,cal}$**	**R^2**	**$Q_{e,exp}$**
Nitrate	1	0.41	0.024	0.99	25.8	0.03	0.99	0.02
	5	0.23	0.9	0.89	4.18	0.01	0.94	0.09
	10	0.21	0.2	0.97	1.7	0.18	0.98	0.16

Intraparticle diffusion model fits suitable to adsorption data as proceeds in two phases, first adsorption of nitrate onto active sorbent's surface, second indicated slow absorption. Nitrate sorption is found higher in initial phase but, much slower as compare to 2nd phase adsorption. While in both phases, nitrate is penetrated into bio-composite matrix resulted underneath surface adsorption. Initially adsorption is most intensive as pointed by high k_{d1} value [23]. Being lower in molecular mass, nitrate showed higher rate of adsorption owing greater penetration in the bio-composite skeleton. Then corresponding nitrate adsorption evolved into 2nd phase with significant lower rate after 60 min and ended as shown in **Table-3**.

Table-3: Adsorbate diffusion rate constants from intra-particle diffusion model

Sorbate	**Molarity** (mM)	**First phase of sorption**			**Second phase of sorption**		
		k_{d1} (mmol/g $min^{-0.5}$)	**Time** (seconds)	R^2	k_{d2} (mmol/g $min^{-0.5}$)	**Phase Time** (seconds)	R^2
Nitrate	1	0.01	300	0.99	0.0007	2400	0.94
	5	0.03	600	0.95	0.0088	3000	0.98
	10	0.04	1500	0.98	0.013	0360	0.85

2.8. Adsorption study: The maximum adsorption capacity can be obtained from analysis of adsorption isotherms of nitrate sorption onto graphite doped chitosan bio-composite. The adsorption data obtained from experimental study were compared using the heterogeneous Langmuir's and Freundlich models as shown in **Figure**-2. But, experimental data best fits to Langmuir than other isotherm models. In Langmuir adsorption nitrate binds onto active sites of adosrbent via monolayer chemisorptions: sheer physical electrostatic interactions and hydrogen bonding. Nitrate and adsorbent sites not interact mutually instead monolayer formation at active centres. Absorbed nitrate mass found to be influenced by maximum sorption capacity Q_{max} and by sorbate affinity to sorbent K_c. Isotherm shape and relatively low K_c value stated nitrate sorption is largely depend on their initial concentration in solution.

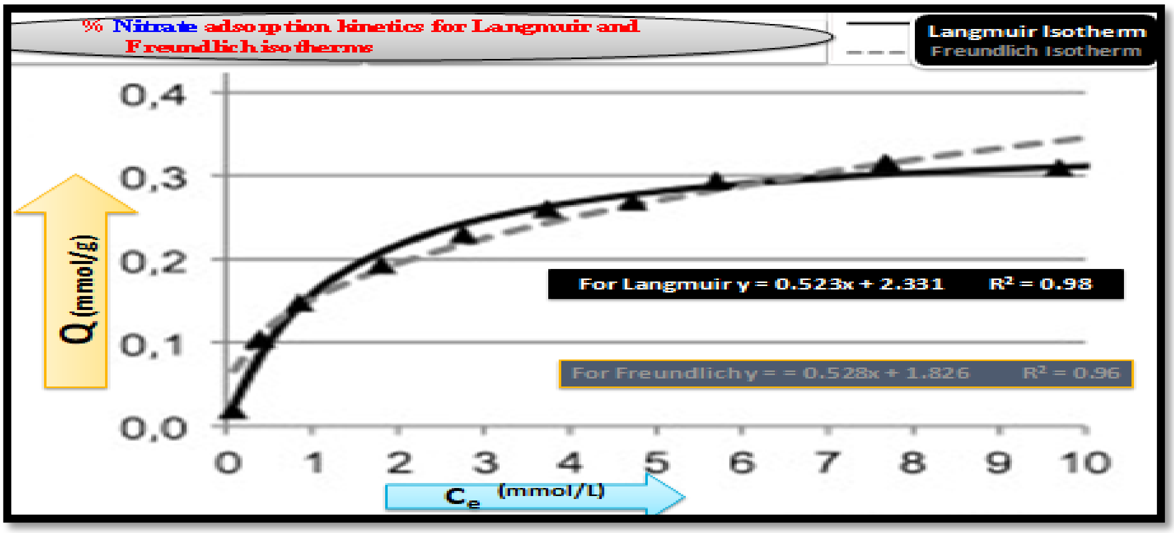

Fig-2: Langmuir and Freundlich adsorption isotherms plots for nitrate removal from water.

Isothermal adsorption constants and sorption capacities are evaluated from Langmuir's and Freundlich adsorption model analysis as summarized in below **Table-4**.

Table-4: Langmuir's and from Freundlich Constants determined at same conditions.

Adsorbate	Langmuir model				Freundlich model		
	Q_{max}(mmol/g	Q_{max}(mg/g	K_c (L/mmol	R^2	n	K	R^2
Nitrate	0.310	4.0	0.81	0.98	0.36	0.15	0.96

2.9. Comparative nitrate adsorption onto diverse adsorbents: The comparative adsorption capacity/efficiency of literature reported various adsorbents used for of effectiveness nitrate anions sorption with graphite doped chitosan bio-composite are shown in below **Table-5**. Sorption capacity of 1 g/L of adsorbent reached 1.2 mmol of all nitrate. Amid the used adsorbents for nitrate sorption, chitosan showed highest affinity reached onto sorption sites of adsorbent as hydrogels. Among the literature reported aand synthesized chitosan sorbents, comparative highest affinity to nitrate is found for graphite doped chitosan sorbents [11-17]. Graphite doped chitosan bio-composites were effective for nitrate sorption from water. Effectiveness of NO_3^- sorption onto chitosan sorbents increases along with a decreasing pH and lowest pH=4 and acidic conditions enhances its sorption capability. Nitrates sorption at lower pH, i.e. pH 2-3, requires the use of cross-linked chitosan which is resistant to dissolution at low pH may significantly increase sorption capability of adsorbent higher compared to unmodified/pure chitosan [14,19-23]. An advantage of doping onto chitosan skeleton enhanced its high sorption effectiveness in a wide pH range (pH 2 - 8). Kinetics of nitrates sorption onto doped chitosan is best described with the pseudo-second order model and intraparticle diffusion model points to three stages of nitrate sorption [11]. The equilibrium time of the sorption process for doepd chitosan composites reaches 60 min, but most nitrates adsorbed within first/initial 30 minutes of adsorption process.

Table-5: Comparative adsorption capacity of various adsorbents for nitrate sorption

SN	Type of sorbent	Maximum sorption capacity (mg/g)	Initial pH
1	Chitosan cross linked epichlorohydrin	38.47	3.0
2	Chitosan cross-linked glutaraldehyde	34.99	3.0
3	Chitosan hydrogels/beads	12.71	4.0
4	Chitosan-coated Zeolite	10.39	5.0
5	Activated Carbon (Commercial)	1.22	6.0
6	Graphite doped chitosan	30.1	3.5
7	Chitosan gels	25.84	4.0
8	Chito hydrogels	39.90	4.0
9	Soil (schist)	3.62	6.5
10	Corn bio-char	0.17	7.4
11	Nano-Al_2O_3	5.48	4.4
12	Undoped/Pure Chitosan	4.1	4.0
13	20% Graphite dope chitosan (This study)	37.2	4.0

III. Results and Discussion

3.1 Adsorbent Characterization

i) Scanning Electron Micrographic images (SEM): Scanning electron micrographic images of graphite doped chitosan bio-composite adsorbent indicated porous morphology with pores of different sizes/shapes with flaky, smooth, shiny appearance and some voids/cavities, where graphite entered chitosan skeleton giving high surface area required for adsorption as in below **Figure-3**.

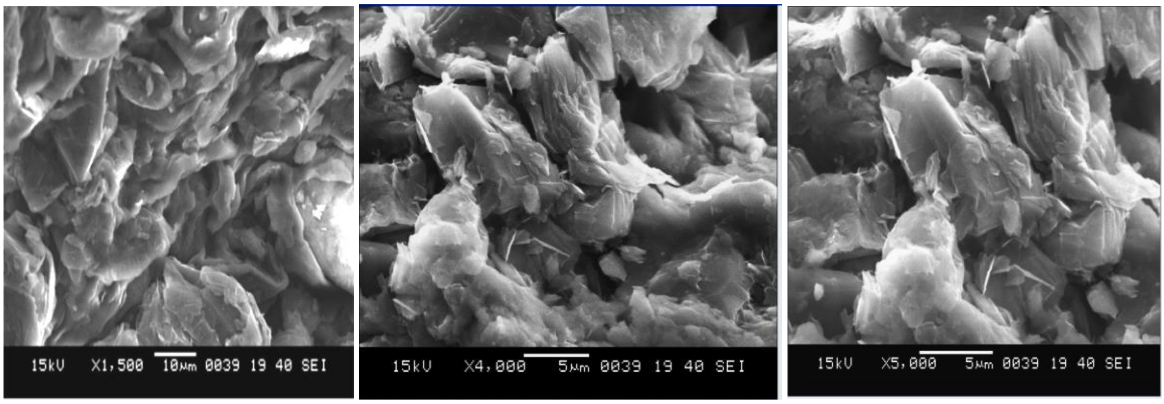

Figure-3: SEM reflections at different magnification (a) 1500 X (b) 4000 X (c) 5000 X

ii) XRD images: X-ray of chitosan, graphite and graphite doped chitosan is shown in **Figure-4 (a, b** and **c)** respectively. Diffraction pattern of chitosan exhibited broad peak at $2\theta = 20°$ owing d- spacing = 4.2 Å as characteristics of semi crystalline nature [20]. Very small peak at $2\theta = 20.74°$ and peak at $2\theta = 20.2°$ are broadened due to amorphous nature of chitosan and matches with reported literatures [14]. X ray diffraction peak appeared at $2\theta = 26.5°$ indicated 3.35 Å d- spacing as the typical characteristic of graphite [19]. X ray diffraction pattern peaks obtained at 2θvalue 26.5 of graphite doped chitosan bio-composite showed formation of single phase composite. Whereas the X ray broad peak observed at $2\theta = 20°$ due to decrease in intensity after doping graphite in chitosan framework also confirms well doping in chitosan frameworks. Predominant peaks of graphite besides small peak of chitosan have appeared in resultant graphite doped chitosan matrix/bio-composite adsorbent implied doping effectively offers supportive proactive sites at adsorbent surfaces.

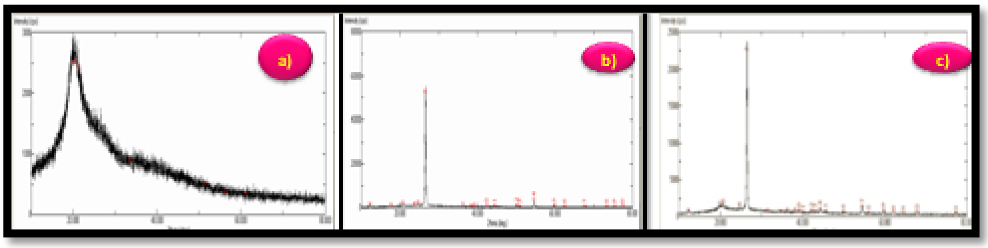

Figure-4: Powder XRD pattern of (a) chitosan (b) graphite (c) Graphite doped chitosan.

iii) FTIR analysis: FTIR of chitosan, graphite and graphite doped chitosan before and after nitrate adsorption are shown in **Figure-5.** IR band at 3695 cm^{-1} and 3073 cm^{-1} are due to stretching vibration of –OH and at 2876 cm^{-1} and 2800–2950 cm^{-1} are assigned to hydroxyl functionality of chitosan while peaks at 1667 cm^{-1} for amide -C=O stretching and at 1152 cm^{-1} for bridge-O-stretching**.** While bending vibrational modes are represented in FTIR peaks for methyl group and C-O-H stretching found at 1375 cm^{-1}, 1434 cm^{-1} and 1262 cm^{-1} respectively. The broad peak at1077 cm^{-1} is due to C-O stretching in C-O-H, C-O-C and CH_2OH linkages of chitosan [12, 17-21]. FTIR peak at 1667 cm^{-1} for C=O stretching is lost and attributed to graphite doping into amide of chitosan. Similarly C-H stretch gets remarkably shifted low at 1367 cm^{-1} than typical characteristics 1375 cm^{-1}.These chitosan and graphite polymers found doped well which consequently alters characteristic FTIR peaks via interactive grafting. Spectra of graphite doped chitosan before and after nitrate adsorption showed peaks either decreased/disappeared in IR intensity pattern due to nitrate adsorption.

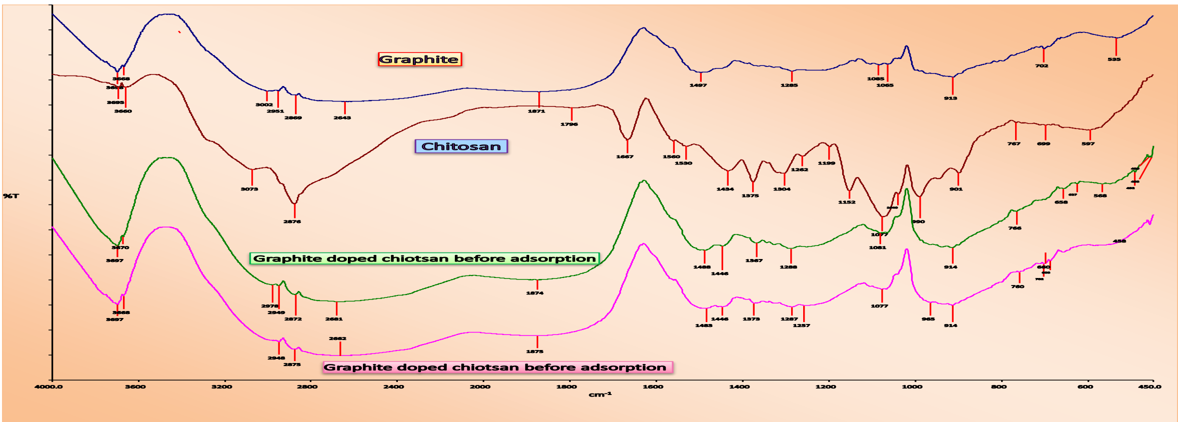

Figure-5: FTIR spectrum of (a) graphite, (b) chitosan, (c) Graphite doped chitosan composite before adsorption (d) Graphite doped chitosan after adsorption.

iv). Determination of equilibrium time: Time require for attaining the adsorption equilibrium was determined at optimized pH for nitrate sorption. Nitrates sorption was conducted in 100 mL Erlenmeyer flasks placed on mechanical shakers. The samples solutions taken 50 mL were analysed for residual nitrate concentration every after 5, 10, 15, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210 and 240 minutes of time intervals. The parameters of analyses of pH value effect on the effectiveness of nitrate sorption are shown in **Table-6**.

Table-6: Varied parameters effect on effective nitrate adsorption on adsorbent

Sorbent	Sorbent weight g/L	Optimized pH	Solution [mL]	Nitrate conc. [ppm]	Sorption time [min]	Stirring speed rpm	Removal efficiency	Temp/ Pressure
Chitosan dope graphite composite	1	4.0	50	5	240	200	94	NTP
	1	4.0	50	10	240	200	88	NTP
	1	4.0	50	15	240	200	79	NTP
	1	4.0	50	20	240	200	71	NTP
	1	4.0	50	25	240	200	66	NTP
	1	4.0	50	50	240	200	60	NTP

v) Effect of pH: Adsorption of nitrate from water was examined at pH range 2 to 10 and the effective adsorption decreases with increasing initial pH of solution as shown in **Figure-6**. Literature reports similar tend reported for nitrate adsorption by polymer-chitosan composites [12-14]. Nitrate sorption efficiency of graphite doped chitosan bio-composite depends on electrostatic attraction between proactive cationic/protonated amine sites of adsorbent. Since, amine protonation enhances at low/acidic pH = 3-4.5 thus resultant nitrate sorption increases corresponding as changes pH > 4 or pH < 4. At extreme acidic pH > 3, nitrate adsorption is futile onto adsorbent surfaces, also at basic pH range 7-10 low nitrate sorption is due to attenuation of negative charge that imparts electrostatic anionic repulsion to nitrate and ultimately prevent adsorption in alkaline condition besides deactivation of chitosan proactive surface functionalities. At alkaline pH counter anion OH^{-} compete nitrate at sorption centres of bio-composite resulted low sorption. At pH < 3.5 electrostatic forces strongly retards biocomposite dissolution, so sorption is disqualified due to weaker electrostatic interactions. In pH range 3 to 4 nitrates suppress electrostatic interactions onto protonated amine as distributed among few proactive sites of adsorbent induced dispersive elevated adsorption. Thus graphite doped chitosan own vast influence of varying pH during nitrate sorption.

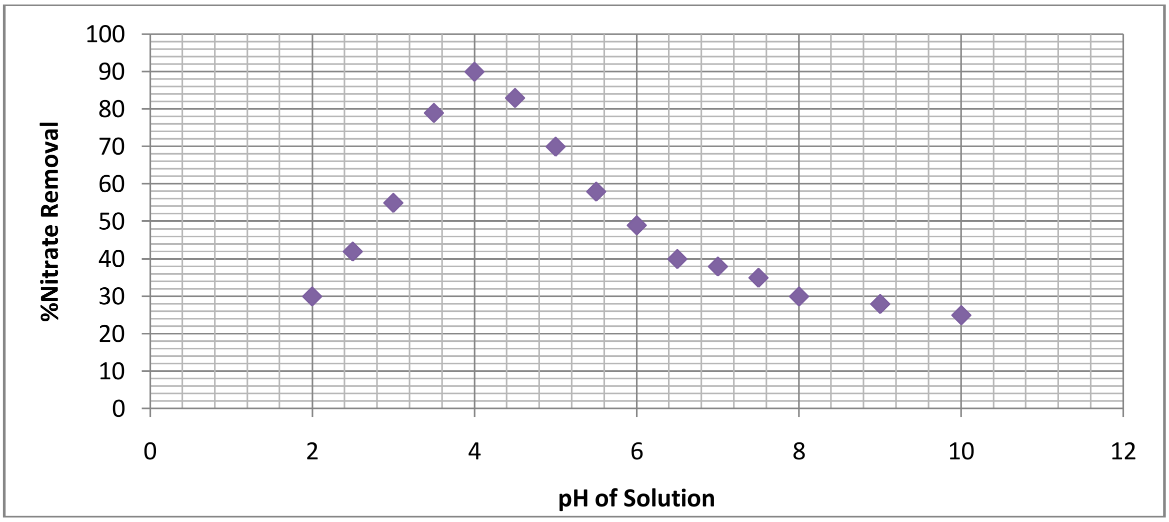

Fig-6: pH effect on effective nitrate sorption onto graphite doped chitosan biocomposite

vi) Effect of graphite doping: Graphite: chitosan content/doping ratio has been optimized for removal of nitrate of water. Hence, assorted graphite contents of 5 % to 30 % (w/w) were varied for doping in chitosan skeleton. However, 20 % graphite doping ratio was found optimum for nitrate removal from water at desired pH=4. Rather, higher than 20% graphite doping/ratio encourages leaching through the resultant bio-composite at the operating pH conditions, besides nitrate permissible limit in treated water is achieved with mere 20 % graphite loading/doping onto chitosan skeleton.

vii) Effect of adsorbent dose: Bio-composite/adsorbent amount/dose found to affect resultant nitrate sorption as shown in **Figure-7**. As dose/amount gets increased the nitrate adsorption establishes elevation but, loading capacity gets gradually decreased. But, the maximum nitrate removal capacity gets elevated/per unit mass of adsorbent since more adsorbate/adsorbent ratio facilitates till adsorbent dose 1 g/L, but further higher dose not showed appreciable progress in nitrate removal.

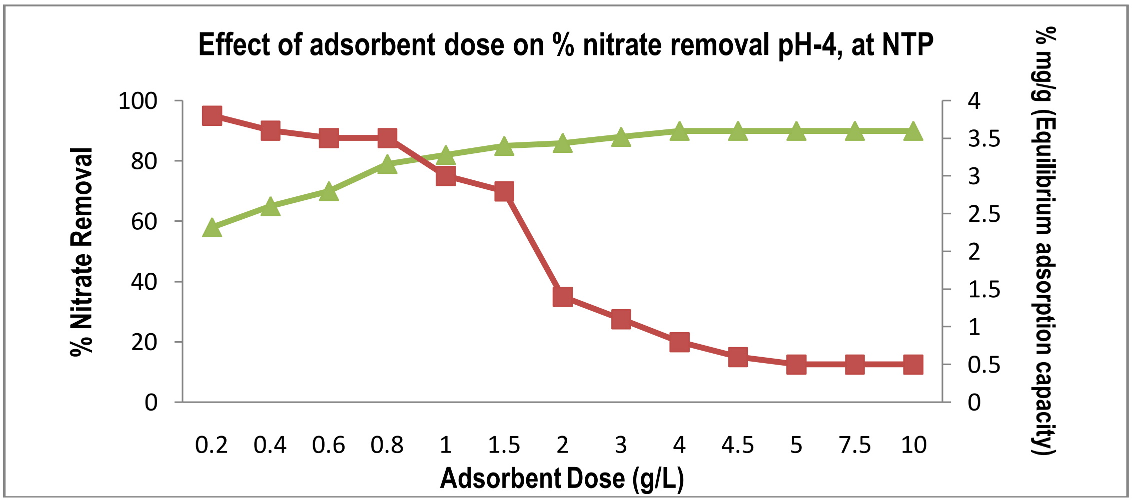

Figure-7: Effect of adsorbent dose on nitrate removal from water at NTP.

viii) Effect of agitation/shaking speed: In such batch adsorptions the agitation/shaking speed is found to affect nitrate adsorption across the external boundary film distribution through the bulk solution. Hence, agitation/shaking speed was varied in range of 50–350 rpm for adsorption experiments. At the start, nitrate adsorption found lower at 50, 100 and 150 rpm, but enhanced at 180 rpm and remains steady at 200 to 250 rpm, the optimized agitation speed is kept at 250 rpm. This agitation speed also attributes little boundary layer resistance and imparts high mobility for the sample ions in solution phase.

ix) Regeneration/desorption Study: Saturated/used bio-composite adsorbent was regenerated via desorption performed at pH > 7 after every experimental cycle. Nitrate anions bind onto amine/hydroxyl/carboxyl of bio-composite via electrostatic forces which gets severely weaken at pH > 7 due to anionic OH^- competitive adsorption. Literature also reports decreasing nitrate removal at **pH > 7** due to inactivity of proactive sites in bio-composite adsorbent. Besides at basic **pH** > 7, chemisorptions phenomenon which gets decreased due to deprotonation of bio-composite surfaces [20]. This, chitosan doped graphite adsorbents is reused up to 5 cycles of adsorption with moderate reduction in removal efficiency.

3.2. Nitrate adsorption Mechanism: Proponent nitrate mitigation occurred through efficient adsorption phases, namely nitrate diffusion to surface from bulk across boundary layer and external mass transfer followed by adsorption onto proactive surfaces of bio-composite; and adsorbed nitrate is exchanged with counter structural elements inside matrix as reassigned via intra particle diffusion in internal pores of adsorbent [14-23] as shown in **Figure-8**.

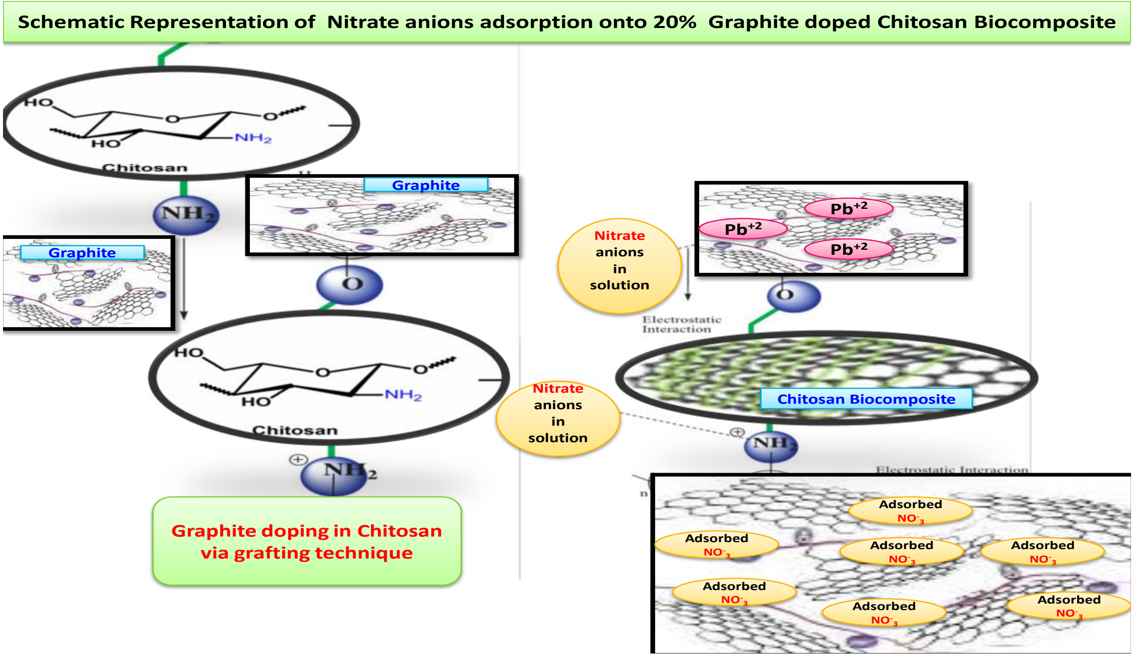

Figure-8: Adsorption phenomenon of nitrate anions onto graphite doped chitosan

IV. Conclusion

The developed 20% graphite doped chitosan biocomposite is highly effective and simple to use for abatement of nitrate from water and achieve its stringent limit without affecting the quality and aesthetic parameters of treated water. The analytical characterization of synthesized adsorbent showed that graphite's laminar layers get fabricated onto -NH_2 /-OH of chitosan and improved its compressive strength, thermal stability and obvious adsorption of nitrate from water. Following conclusions are drawn from this de-nitrification study.

- Bio-composites is an effective adsorbent for nitrate removal from water at NTP and optimized moderate acidic pH=4. Nitrate adsorption is ineffective above $pH > 4.5$ due to attenuation of zero point charge of chitosan ($pH_{ZPC} = 7.6$) and showed maximum nitrate removal capacity at adsorbent dose of 1g/L beside achieve nitrate permissible limit of 10 ppm in treated water.
- Experiment data indicated tangibly preferable nitrate sorption depends on specific sites rather than BET surface area at adsorbent surfaces than other anionic impurities.
- Adsorption isotherms are somewhat favourable and almost linear shown initial rapid sorption gets slow down at approaching equilibrium which follow the pseudo-2nd order better than 1st order kinetic model.
- Nitrate removal occur through bio-sorption as ever prefer due to its economy and also by virtue of fewer sludge/waste generation and bio-adsorbents is better than other reported adsorbents due to special features viz; inherent biodegradability, non-toxicity, besides owing flexibly adoptable graphite doping.
- 20% Graphite doping in chitosan imparts surface modification and transformed flexible chitosan-graphite skeletons into resultant immobilized matrix owing proactive functionality alterations like hydroxyl/carboxyl/amide groups, which collectively improved nitrate adsorptions onto elevated resultant surface area.
- Doping intercalates hydrophobic polycationic inter-layers and impose great anion exchange capacity for nitrate despite of chlorides and sulphates anionic impurities in acidic pH sustainably exchange proton and ultimately reported elevated nitrate removal efficiency.
- Adsorption gets influenced by graphite: chitosan impregnation ratio, and synthesized bio-composite performs multifaceted functions besides facilitated nitrate mass transfer yields efficient biosorption over other conventional adsorbents

- The bio-composite can be reused till fivefold nitrate adsorption cycles. Rather, this de-nitrification of water is preferred as tertiary stage treatment after bio-treatments.

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