

This chapter describes different materials used during the study, methodologies adopted for preparing them, different physicochemical, spectroscopic and theoretical tools used for characterization and evaluation of their performance.

2.1 Materials used

Table 2.1 Chemicals used during the study along with the name of manufacturers

Serial No.	Chemical	Suppliers
1	Chitosan	Sigma Aldrich
2	FeCl ₃ .6H ₂ O	-do-
3	FeCl ₂ .4H ₂ O	-do-
4	NaOH pellets	Merck India
5	Glutaraldehyde 25% (w/v)	-do-
6	Hydrochloric acid	-do-
7	Acetic acid	-do-
8	Sodium arsenate heptahydrate	Sigma Aldrich, USA
9	De-ionized water	Millipores.A.S.67 120 MOLSHEIM, FRANCE
10	Monmorillonite-K10 clay	Sigma Aldrich, USA
11	TiO ₂ (mixture of rutile and anatase)	-do-
12	Starch polymer	SRL, India
13	N-cetyl-N,N,N – trimethyl ammonium bromide	LOBA Chemie, India
14	Ethanol	Merck India
15	Acetone	-do-
16	Roots of water hyacinth	Local pond of Tezpur Unievrsity
17	Sodium metaarsenite	Sigma Aldrich, USA
18	Citric Acid	Merck India
19	Glycidal Methacrylate	-do-

20	Ethylene diamine	-do-
21	K ₂ S ₂ O ₈	-do-
22	Fe(NO) ₃	-do-
23	OMMT Nanoclay	Merck India

All other reagents used for the study were of analytical grade

2.2 Experimental Methods

2.2.1 Synthesis of Chitosan Based Nanocomposite

2.2.1.1 Chitosan Coated Magnetite Nanocomposite (CTN)

CTN composite was prepared in two steps by a simple ex-situ method. Initially, magnetite (FeN) particles were synthesized by co-precipitating Fe²⁺ and Fe³⁺ (2:3 w/w) ions followed by treating under hydrothermal condition [1]. In the present study, sodium hydroxide solution was used for precipitation. 1% (w/v) chitosan (CT) solution was prepared simultaneously by dissolving requisite composition (CT:FeN~1:8) of the polymer in 1% (v/v) acetic acid solution. To that solution, FeN nanoparticles in suspension form was poured and mixed for 2 h under high stirring rate. CT was then precipitated by NaOH solution. Temperature of the reaction vessel was brought down to below room temperature. Then Glutaraldehyde solution was added dropwise to the mixture under high stirring condition. The temperature was again raised gradually to 50 °C and the reaction was continued for another 2 h under continuous stirring, which was then decreased to room temperature. The nanocomposite thus formed was filtered, washed with de-ionized water, dried and kept ready for subsequent applications.

2.2.1.2 Preparation of Ct/Glu and MMT/Ct/Glu

Two types of materials were prepared for the batch adsorption test; one without nanoclay (Ct/Glu) and other with the clay mineral (MMT/Ct/Glu) with simplified Ionic-Gelation technique [2]. In this technique ionic polymer is treated with oppositely charged ion to initiate cross linking. These interactions of polyanion with cations cannot be completely explained by the electro-neutrality principle. The three dimensional structure and presence of other groups influence the ability of cations to conjugate with anionic functionalities. 1g of chitosan polymer was dissolved in 200 mL of 1% acetic acid solution under magnetic stirring. It was then transferred to a 500 mL round bottom

(RB) flask and re-precipitated by adding 0.1 M NaOH solution dropwise under high mechanical stirring. For Ct/Glu type of adsorbent, a calculated amount (5% w/w) of glutaraldehyde (0.185 mL/g of chitosan) crosslinker was added to the precipitate and allowed to cross link at 45 °C. In the second case, clay (10% w/w of polymer) solution dispersed in water (24 h) was added to the acidic solution of chitosan, shaken vigorously with mechanical stirrer for 2 h and sonicated (UP 200 S, Hielscher-Ultrasonics-GmbH, Germany) for another 30 min. Then, precipitation was done by dropwise addition of NaOH solution under high stirring condition. This was followed by drop wise addition of glutaraldehyde crosslinker and allowed for cross linking under similar condition as mentioned in the former case. The reddish brown precipitate of nanocomposite was washed several times with double distilled water to remove excess NaOH, left, if any in the reaction mixture, dried and kept for subsequent use.

2.2.2 Synthesis of Starch Based Nanocomposite

2.2.2.1 Methods of Preparation of Starch Coated TiO₂ Nanocomposite

Coating of starch over TiO₂ particles was carried out in two steps following the method reported by Deka and Maji [3]. Initially TiO₂ was modified with CTAB and then was coated with starch. It makes the component materials more compatible with each other which will be helpful for the better efficiency as well as stability of sorbent during regeneration.

2.2.2.1.1 Preparation of CTAB modified TiO₂ (CMT) Nanoparticles

1.0 g of TiO₂ was taken in a round bottomed flask containing 1:1 ethanol–water mixture. It was fitted with a spiral condenser and kept at 80 °C for 12 h under magnetic stirring. In another similar set up, 1.2 g of CTAB was refluxed with 1:1 ethanol–water mixture at 80 °C for 3 h. This mixture was poured into the dispersed TiO₂ solution mixture and was stirred again for another 6 h at 80 °C. It was then filtered and washed with lukewarm deionised water several times and dried in oven at 45 °C. Finally, the material was grinded and stored in desiccator to avoid moisture absorption.

2.2.2.1.2 Preparation of starch coated CMT nanocomposite (SPC)

1.0 g of CTAB modified TiO₂ (CMT) was dispersed in 250 mL beaker under continuous magnetic stirring for 1 h. It was then sonicated for 30 min to completely disperse the CMT nanoparticles in the solvent.

In the mean time, a solution of starch was prepared by dissolving 0.5 g in 50 mL of hot water (80 °C). The CMT solution was then mixed with the starch solution and stirred for another 1 h. Starch typically has many hydroxyl groups on them, which are polar. These hydroxyl groups interact with the polar ends of CTAB and form a coating around them. This mixture was then poured slowly into acetone under stirring conditions in order to precipitate SPC particles.

The temperature of the beaker was brought down below room temperature. Now, glutaraldehyde solution (5% w/w) was added to the mixture containing SPC particles under magnetic stirring. Temperature was again raised gradually to 50 °C and the reaction was continued for another 2 h under continuous stirring condition, then decreased to room temperature. The nanoparticles thus formed was filtered, washed with de-ionized water, dried and kept ready for subsequent applications.

2.2.2.2 Preparation of Starch/OMMT/FeO(OH) nanohybrid

Three steps were involved during the preparation-

1. Grafting of starch
2. Amination of grafted starch
3. Preparation of the nanohybrid

Starch and GMA were refluxed together in 1:2 molar ratios in presence of initiator $K_2S_2O_8$ (6mmolL^{-1}) at around 60 °C for 3 h in aqueous medium under N_2 atmosphere. This was then precipitated in acetone followed by filtration to obtain the GMA grafted starch, which was oven dried and grinded to powder form.

The grafted starch was aminated by refluxing with ethylene diamine (EDA) under continuous stirring for 12 h at 90 °C. 0.1 M HCl solution was used as activator during the process. The material thus obtained was dried in oven and then grinded to obtain it in powdered form.

In the third step, calculated amount of amminated starch was dispersed in de-ionized water to which the suspension of OMMT clay [previously dispersed in aqueous medium (24 h stirring followed by sonication)] was poured under stirring condition. The mixture was sonicated again before going to the next step. In the meantime, a 0.06 M $Fe(NO_3)_3$ solution was prepared which was mixed with the previous one and kept under stirring for another 1 h. The mixture was then precipitated by drop wise addition of 0.1 M NaOH till completion of precipitation. The whole mixture was heated at 50-70 °C and then filtered. After that, it was dried and then grinded to get it in powdered

form and then sieved to 100 mesh size (100 openings/in²). Three different variations of materials containing 5%, 10% and 20% (w/w) OMMT clay were prepared.

2.2.3 Synthesis of *E. Crassipes* Biomass based Composite

2.2.3.1 Preparation of Citric acid crosslinked root powder (RP)

The collected roots of water hyacinth were initially washed several times with water. Then it was soaked in 0.1 M NaOH solution for several hours and washed with surfactant. Finally, the roots were washed with distilled water and allowed to dry at about 40 °C in hot air oven. The dried roots were grinded to powder and sieved to 100 mesh size and kept for subsequent uses.

Crosslinking of root powder was carried out with citric acid in presence of TiO₂ catalyst by following the method of Okeil with little modification [4]. In the present study, the crosslinking was tried to carry out in water medium. Initially three different variations of citric acid solutions viz. 1%, 5% and 10% (w/w of water hyacinth root powder) were prepared. Now, 0.6% (w/w) of TiO₂ was dispersed to each solution under stirring condition. Then same amount of root powder was poured into each mixture under stirring conditions and the temperature of the mixture was gradually increased to 90 °C. It was allowed to react for 2h, then centrifuged, filtered, washed several times with de-ionized water to remove unreacted citric acid, if any, dried and grinded to powder form for subsequent uses.

2.2.3.2 Preparation of Chitosan/Root powder Composites (CTRP)

The collected roots of water hyacinth were initially washed several times with water. Then it was kept in 0.1 M NaOH solution for several hours and again washed several times with surfactant. Finally the roots were washed with distilled water and allowed to dry at about 40 °C in hot air oven. The dried roots were grinded to powder and sieved to 100 mesh size and kept for subsequent uses. Simultaneously, a chitosan solution was prepared by dissolving requisite amount of it in 1% (v/v) acetic acid solution. Then different amount of root powder (in 1:0.25, 1:0.5 and 1:1 ratio w.r.t. Chitosan content) was added to it to prepare three composite systems. The mixture was then stirred vigorously for half an hour. NaOH solution was then added to the above mixture to precipitate the chitosan completely. This was followed by the addition of glutaraldehyde solution under cold condition. The temperature was then gradually increased to 50-55 °C and allowed to crosslink for another 3h. Finally, it was filtered

and washed with de-ionized water until it became neutral and then the sample was dried in hot air oven at about 60 °C.

2.3 Methods of Characterization and Measurements

2.3.1 Fourier Transform Infra-red (FT-IR) Spectroscopy

FT-IR was used to study the interactions among different component materials while preparing a composite. It is based on the shifting of absorption band, change in intensity or appearance of new bands. Here, Fourier Transform Infrared spectra (FTIR) were recorded in the range of 4,000-500 cm^{-1} in a Nicolet (model: Impact- 410) spectrophotometer. The samples were mixed with KBr to prepare a pellet and then FT-IR spectra were recorded. The probable sorption of arsenic on the sorbent material was also predicted by FT-IR analysis.

2.3.2 X-Ray Diffraction (XRD) Study

Crystallinity of polymer nanocomposites with respect to component materials was studied using XRD. It provided information about degree of crystallinity of component polymers, nanomaterials, etc. The interlayer spacing of the nanoparticles could be calculated from the characteristic peak of the X-ray diffractogram by using Bragg's equation, $2d \sin\theta = n\lambda$, where θ is the diffraction angle, λ is the wavelength of the x-ray, n is the order of diffraction and d is the interlayer spacing. If the polymer had some crystalline regions, then the interaction of X-ray resulted a sharp peak in the diffractogram, which is a plot of peak intensity versus 2θ .

Different materials in present study were characterized by powder X-ray diffraction (Rigaku, miniflax, UK) analysis. The measurement conditions were taken as follows: anode material=Cu; K-alpha, $\lambda=1.54 \text{ \AA}$, and scanning rate $2^\circ/\text{min}$ with an angle ranging from $2\theta=4^\circ$ to 70° .

2.3.3 Dynamic Light Scattering Analysis (DLS)

Particle size and zeta potential were calculated using particle size, zeta potential and molecular weight analyser (Nanotrec Wave).

2.3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate) or as a function of time (with constant temperature and/or constant mass loss). TGA is commonly used to determine the characteristics of materials that usually exhibit mass loss due to decomposition, oxidation or loss of volatiles (such as moisture). TGA thermograms were recorded for all samples using a thermogravimetric analyser (Metler TA 4000) at a heating rate of 20 °C/min upto 600 °C under N₂ atmosphere.

The polymeric content incorporated could be calculated using the following equation (Zhang *et al.* 2010).

$$\text{Chitosan content (\%)} = W_s (\%) - W_n (\%) \quad 2.1$$

Where, W_s is the weight loss (%) from 100 °C to 500 °C for composite and W_n is the weight loss (%) for particles/nanoparticle.

2.3.5 pH Measurement

The pH of the arsenic solutions was adjusted using NaOH (0.1 M) and/or HCl (0.1 M) solutions as and when required and measured by Cyberscan pH 510 (Eutech) instrument. Zero point charge pH was calculated using pH drift method [5]. For that arsenic solutions were taken in different beakers and pH of each solution were adjusted in the range under interest by using 0.5 M HCl or 0.5 M NaOH. Then same amount of adsorbent were added to different beakers and equilibrated for 24 h. The final pH (pH_f) was measured and difference of final and initial pH ($pH_f - pH_i$) was plotted against the initial pH (pH_i). Point of interaction of this $pH_f - pH_i$ curve with the straight line drawn from zero along y axis parallel to x-axis is taken as the pzc for the particular material. Influence of pH on adsorption was studied only to have idea about the electrostatic nature of sorption and reaction mechanism. Hence, despite the better result in acidic pH, rests of the studies were carried out at normal pH

2.3.6 SEM-EDX Analysis

The surface morphology was studied by Scanning Electron Microscopy (SEM). The phase domain size, number of phases, etc. present in the surface of materials could be detected by SEM. In SEM, images are produced by the detection of secondary electrons, which are emitted from the surface of the sample due to excitation by the primary electron beam under high vacuum. Samples were deposited one by one on a

brass holder sputtered with platinum for taking scanning electron image (Model: JEOL JSM-6390 LV). The surface morphologies of the samples were studied at an accelerated voltages of 15-20 kV.

Energy Dispersive X-Ray (EDX) from the same instrument was used for the elemental analysis. It depends on the interaction of a source of X-ray excitation and a sample. Its characterization capabilities lie in the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its X-ray emission spectrum.

2.3.7 DC Susceptibility Measurements

Magnetic phase transitions were measured as a function of temperature varying DC magnetic susceptibility reader (Bartington instrument, MS2/MS3).

2.3.8 Atomic Absorption Spectroscopy (AAS)

It is another analytical tool which is based on Beer-Lambert law and it can predict the concentration of different elements on the basis of absorbance focused beam of light. In the present study, As concentrations were measured by using the vapour mode of Analyst 200 Atomic Absorption Spectrophotometer (Perkin Elmer). All the measurements were based on integrated absorbance and performed at 193.7 nm using a quartz tube analyser (Perkin Elmer) at an atomization temperature of 2000 K. Calibration curves were prepared by taking four standards viz. aqueous solution of arsenic (V) 10, 20 30, 40 $\mu\text{g/L}$. The detection limit of the flame mode is 0.12 mg/L and vapour mode is 0.05 $\mu\text{g/L}$.

2.3.9. Transmission Electron Microscopy (TEM)

The distribution of nanomaterials within polymer matrix was studied by Transmission electron microscope (JEOL JEM-2100) at an accelerating voltage of 200 kV.

2.3.10 Inductively Coupled Plasma Spectrophotometer

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a

particular element. It is a flame technique with a flame temperature in a range from 6000 to 10000 K. The intensity of this emission is indicative of concentration of element within the sample. In present case, OPTIMA 211 DV (Perkin Elmer) was used to measure the inorganic Arsenic species irrespective of its oxidation state.

2.4 Batch Adsorption Test for Arsenic

Stock solutions containing 1000 mg/L of As(III)/As(V) were prepared by dissolving requisite amount of sodium meta arsenite or sodium arsenate heptahydrate required in 1000 mL de-ionized water. The stock solution was diluted in steps to obtain standard solutions containing different concentrations of arsenic solution. Batch experiments were carried out in a mechanical shaker at an agitation speed of 160 rpm at neutral pH in 100 mL conical flasks, at room temperature. After agitation, sorbent/solution mixture was allowed to stand for 12 hours and supernatant were taken for the centrifugation and/or filtration. Arsenic concentration left in the aliquot was determined by atomic absorption spectrophotometer. For the magnetic nanoparticles instead of filtration, separation of the particles was done by using a bar magnet.

The Removal rate (R%) and equilibrium adsorption capacity (q_e) were calculated using the Eq. 2.1 and Eq. 2.2, respectively [6]

$$\%R = \frac{C_o - C_t}{C_o} \times 100 \quad \text{Eq. 2.2}$$

$$q_e = \frac{(C_o - C_e)V}{M} \quad \text{Eq. 2.3}$$

where, q_e (mg/g) is the equilibrium adsorption capacity, C_o and C_e are the initial and equilibrium concentration (mg/L) of arsenic in solution, V (L) is the volume and M (g) is the weight of the adsorbent.

2.4.1 Effect of Experimental Conditions on Removal Efficiency

Effect of material doses, nature of materials, agitation time, initial ion concentrations, pH and competition ions on percent removal or sorption capacity for arsenic were tested.

2.4.1.1 Influence of Material Dose

Different materials in present study have different sorption efficiency depending on the sorption sites, surface and nature of sorption. Hence, for a particular arsenic concentration, amount of materials required may vary to show efficient removal. Therefore, for each type of material the influence of increasing material dose on removal rate was determined.

2.4.1.2 Influence of Agitation Time

Time required to reach the adsorption equilibrium is different for different materials. All the studies related to the mechanism like isotherm, kinetics, thermodynamics, etc. of sorption are studied at equilibrium only. Therefore, it was very much essential to determine the time to gain equilibrium. For that a particular concentration of arsenic solution is treated with the sorbent for varying interval of time and sorption capacity for each time interval was calculated.

2.4.1.3 Influence of Initial Ion Concentration

Adsorption is always accompanied by equilibrium and concentration of adsorbate has great influence on the position of equilibrium. Thus, the influence of initial ion concentration on removal efficiency for one type of material was evaluated by subjecting a fixed dose of it to different arsenic concentrations keeping the time of treatment same.

2.4.1.4 Influence of Temperature

Effect of temperature on sorption of arsenic was examined by carrying the sorption in three different temperatures viz. 303, 308 and 313 K. Both removal efficiency and sorption capacity were determined to study the influence of temperature. The thermodynamic parameters were also analyzed on the basis of temperature effect.

2.4.1.5 Influence of pH

Arsenic species exist in different forms (charged or uncharged) depending on the pH conditions. Charge of the sorbent materials also may vary with pH of the solution. pH played an important role on sorption efficiency of the materials. To study the influence of pH, batch experiments were carried for a targeted arsenic solution keeping the material dose and treatment time fix while the pH was varied in the range 2.0-12.0.

2.4.1.6 Influence of Competition Ions

Sorption of arsenic on the presented materials mainly occurs through the functional sites present on the materials, their affinity for arsenic and other ions which may be present in the solution. Thus, there might occur some competition among different ions present in solution for sorption site. To investigate the effect of interfering ions such as PO_4^{3-} , Cl^- and SO_4^{2-} on arsenic sorption, respective sodium salts were added to the arsenic solution before treatment. Phosphate shows similar chemical behavior as that of arsenic and may exist as different ionic species at different pH, as those of arsenic. Phosphate ions exist mostly as diprotonated monoanionic H_2PO_4^- species in the pH range under interest. Gao and Mucci have demonstrated the competition between phosphate and arsenate for sorption site on goethite. Phosphate showed high affinity for goethite and compete with arsenate. The surface complexation of arsenate decreases significantly in competitive adsorption experiments and the decrease is proportional to the amount of phosphate present [7]. Many literatures showed that the influence of sulphate and chloride ions on arsenic sorption, under similar experimental conditions, was very much negligible while that of phosphate was much significant. Hence, in two different cases, in this thesis, sulphate and chloride were taken separately along with phosphate as co-ions.

2.4.2 Kinetics of Sorption Study

Study of kinetics of sorption is very much essential to understand the mechanism of sorption. From kinetic analysis, solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information. Thus, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems. Also, once we have idea about the rate controlling step, proper modification of experimental conditions can be done to have better performance.

Adsorption kinetics were studied with different initial concentrations at equilibrium time and optimized material dose at normal pH. Pseudo first order, pseudo second order and intraparticle diffusion models were applied to study the mechanism of sorption.

The Linear form of a simple pseudo first order kinetic model is [8]

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{k_{ad}}{2.303t} \quad \text{Eq. 2.4}$$

where, q_t is the amount of arsenic adsorbed (mg/g) at time t , q_e is the amount of As(V) adsorbed (mg/g) at equilibrium and K_{ad} is the rate constant of adsorption (min^{-1}). The values of k_{ad} , and q_e were calculated from the slope and intercept of the respective linear plots. In pseudo first order reactions, concentration of one reactant remains constant. The name physisorption was given to this, since the rate-limiting step in this kind of mechanism is diffusion and not dependent on the concentrations of both reactant. If the surface diffusion is rate controlling, the rate of the adsorption will vary inversely with the particle size, the film thickness and with the distribution coefficient.

The linear form of type I pseudo-second-order kinetic models is represented by the following equation [9]

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad \text{Eq. 2.5}$$

where, $t = q_e^2 kt / (1 + q_t kt)$, the amount (mg/g) of As(V) adsorbed on the surface of material at any time t , k being pseudo-second order rate constant ($\text{gmg}^{-1}\text{min}^{-1}$), q_e is the amount adsorbed at equilibrium, and $h = kq_e^2$ ($\text{mgg}^{-1}\text{min}^{-1}$) is the initial sorption rate. In pseudo second order kinetics of adsorption, the chemical reaction is reported as the rate-controlling step and adsorption's mechanism is chemically rate controlling. In this mechanism, the kinetics of sorption should correspond to a reversible second order reaction at low sorbate/sorbent ratios (first order at very low ratios), and two competitive reversible second order reactions at higher sorbate/sorbent ratios.

Adsorption usually occurs via multi steps like transport of adsorbate to solid surface of adsorbent, diffusion of the adsorbate particles through pores of the adsorbent to its interior. The diffusion process is usually slow and it is considered as the rate determining step. The possibility of diffusion of arsenate ions into adsorbent was tested by using the intraparticle diffusion model as represented below [10]

$$Q_t = k_{ip} t^{1/2} + C \quad \text{Eq. 2.6}$$

where, Q_t is the amount (mg/g) at time t , k_{ip} ($\text{gmg}^{-1}\text{min}^{-1}$) is rate constant for intraparticle diffusion, C is a constant which determines the thickness of the boundary layer. Values of K_{ip} and C can be calculated from the Q_t vs $t^{1/2}$ plot.

2.4.3 Isotherm of Sorption Study

Study of Isotherm model is very essential to know about the nature of sorption. In present study, Langmuir, Freundlich and Temkin isotherm models were applied for studying the sorption pattern.

2.4.3.1 Langmuir Isotherm Model

Langmuir isotherm model is based on the assumption that the surface of adsorbent is homogeneous in nature and sorption occurs only in one layer. Mathematical representation for the model is [7]

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad \text{Eq. 2.7}$$

where, q_e is the equilibrium quantity adsorbed (mg/g), C_e is the equilibrium concentration (mg/L), q_m is the maximum adsorption capacity (mg/g) and 'b' is the Langmuir constant.

The separation factor, R_L an important parameter indicating favorability of the adsorption based on Langmuir equation is calculated using equation.

$$R_L = \frac{1}{1 + bC_0} \quad \text{Eq. 2.8}$$

where, b and C_0 have their common meaning. The value of R_L indicates the type of adsorption either to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

2.4.3.2 Freundlich Isotherm model

Freundlich model assumes that the adsorbent surface is heterogeneous in nature and sorption occurs mainly due to weak van der Waals type of interaction. The linear form of Freundlich adsorption equation is represented by the equation [7]

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad \text{Eq. 2.9}$$

where, q_e is the adsorbed amount (mg/g), C_e is the equilibrium arsenic concentration (mg/L), k_f (mg/g) is the Freundlich constant related to adsorption capacity and 'n' is a constant related to energy of intensity of adsorption.

2.4.3.3 Temkin Isotherm Model

This isotherm takes adsorbent-adsorbate interactions into account. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [11]. The Temkin isotherm model is represented by the equation given below-

$$q_e = \frac{RT}{b} \ln A_T + \left(\frac{RT}{b} \right) \ln C_e \quad \text{Eq. 2.10}$$

where,

A_T = Temkin isotherm equilibrium binding constant (L/g)

b = Temkin isotherm constants

R = universal gas constant (8.314 J/mol/K)

T = Temperature at 298 K

q_e and C_e have their common meaning.

Temkin model is useful to study the sorption when the concentration of ion is in intermediate range (~40-400 µg/L). Temkin isotherm constant 'b' is indication of heat of adsorption and can predict the nature of the sorption [12].

2.4.4 Thermodynamics of Sorption Study

The exact nature of sorption process and its feasibility can be studied by knowing the thermodynamic parameters such as energy and entropy and then only the practical applicability of the method can be evaluated. To determine the thermodynamic parameters for sorption of arsenite ions on the prepared material, batch experiments were carried out at three different temperatures viz. 303, 308 and 313 K respectively. The pseudo second order rate constants (k_2) for the sorption process were plotted against $1/T$ as described by Arrhenius equation (Eq. 7) which gave a straight line. From the slope of the straight line the apparent value of activation energy (E_a) was calculated.

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad \text{Eq. 2.11}$$

where, A is Arrhenius temperature independent factor, R is the Universal gas constant (8.314 JK⁻¹mol⁻¹), T is the temperature in Kelvin. Nature of sorption can be described with the help of the value of activation energy; if it lies in the range 5-40

kJmol^{-1} , then the sorption pattern is physisorption type and if it is 40-800 kJmol^{-1} , then it is chemisorption type [13].

The other thermodynamic parameters viz. change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be evaluated by using the following equations

$$K_c = \frac{C_A}{C_S} \quad \text{Eq. 2.12}$$

$$\Delta G^\circ = -RT \ln K_c \quad \text{Eq. 2.13}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{Eq. 2.13}$$

where, K_c is the equilibrium constant, C_A is the amount of arsenite (mol/L) adsorbed on the surface of the material, C_S (mol/L) is the amount remained in the solution. Plot of $\ln K_c$ against $1/T$ gave a straight line, from the slope and intercept of which the values of ΔH° and ΔS° could be determined.

2.5 Reusability Test

The long term usability of the materials for arsenic treatment was examined by regeneration test. The samples were subjected to several cyclic runs and after each run their efficiency and structural integrity was monitored. For that, Desorption of adsorbed arsenic from the sorbent was carried out by digesting with 0.05 M HCl solution. Arsenic treated material was dried and then digested with the extracting solution keeping the solid/liquid in ~1:20 ratio for 24 h at room temperature. After that it was filtered and residue was washed several times with Milli-Q water till it became neutral. Then it was again treated with arsenic solution and subsequent cyclic runs were carried out.

2.6 Computational Modeling Study

Density functional calculations were carried out using DMol³ package utilizing the nonlocal exchange-correlation functional of Perdew et al. [14, 15] (PW91) exchange-correlation functional at the generalized gradient approximation (GGA) level. The van der Waals (vdW) interactions were taken into consideration while performing theoretical calculations, as polymeric structures bind through vdW interactions. Dispersive forces, or van der Waals forces, resulted from the interaction between fluctuating multipoles without requiring the overlap of electron densities [16].

Therefore, dispersion corrected density functional theory (DFT-D) for geometry optimization and frequency analysis was utilized. DFT-D approaches to treat vdW interactions was employed using the Ortmann, Bechstedt and Schmidt (OBS) correction to VWN and DNP (double numerical plus polarization) basis set was chosen for the calculations [17, 18]. The geometries of reactants and the cross-linked product were optimized without imposing any symmetry constraints using all electron spin-unrestricted calculation, indicating electronically open shell system. For the heavy metal Arsenic, the valence electrons were described by double numerical basis set with polarization function and the core electrons were described with local pseudo-potential (VPSR) which accounts for the scalar relativistic effect expected to be significant for heavy metal elements [19]. The structures were fully relaxed and positive vibrational frequencies confirmed the complexes to be at energy minima.

A particular computational technique chosen depends on the desired accuracy (qualitative vs. quantitative), size of the system and available computational resources. Quantum calculations complement experimental studies can assist interpretation of reaction mechanisms - for stable intermediates formed can be modeled. By comparing calculated geometries, relative adsorption energies, vibrational modes, etc., to experimental observations - quantum chemical calculations can help in identifying adsorption complexes. Special focus was given to the type of interaction taking place, complexes formed, which was of utmost importance in the study. It could help in modification of material, to improve its property as As binder. So, Density functional theory (DFT) calculations were chosen to investigate As(V) and As(III) surface complex structures.

2.7 Statistical Analysis

All the data were expressed as mean \pm SD. The statistical analysis of the data was done by Student's t-test using the software SigmaPlot 10.0 for the windows (version 7.0). A value of $p < 0.05$ was considered as significant difference between two values.

References

- [1] Jia, Z., Yujun, W., Yangcheng, L., Jingyu, M. and Guangsheng, L. In situ preparation of magnetic chitosan/Fe₃O₄ composite nanoparticles in tiny pools of water-in-oil microemulsion. *Reactive and Functional Polymers*, 66:1552-1558, 2006.
- [2] Racoviță, S., Vasiliu, S., Popa, M. and Luca, C. Polysaccharides based on micro- and nanoparticles obtained by ionic gelation and their applications as drug delivery systems. *Revue Roumaine de Chimie*, 54:709-718, 2009.
- [3] Deka, B. K. and Maji, T. K. Effect of TiO₂ and nanoclay on the properties of wood polymer nanocomposite. *Composites: Part A*, 42:2117-2125, 2011.
- [4] Okeil, A. A. Citric Acid Crosslinking of Cellulose Using TiO₂ Catalyst by Pad-Dry-Cure Method. *Polymer-Plastics Technology and Engineering*, 47:174-179, 2008.
- [5] <https://groups.google.com/forum/#!topic/sci.chem/0ihYTWpw67M>
- [6] Hena, S. Removal of chromium hexavalent ion from aqueous solutions using biopolymer chitosan coated with poly 3-methyl thiophene polymer. *Journal of Hazardous Materials*, 181:474-479, 2010.
- [7] Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7 M NaCl solution, *Geochimica et Cosmochimica Acta*, Vol. 65, No. 14, pp. 2361–2378, 2001
- [8] Bhatt, A. S., Sakaria, P. L., Vasudevan, M., Pawar, R. R., Sudheesh, N., Bajaj, H. C. and Mody, H. M. Adsorption of an anionic dye from aqueous medium by organoclays: equilibrium modeling, kinetic and thermodynamic exploration. *RSC Advances*, 2:8663-8671, 2012.
- [9] Ho, Y. S. Isotherms for the Sorption of Lead onto Peat: Comparison of Linear and Non-Linear Methods. *Polish Journal of Environmental Studies*, 15:81-86, 2006.
- [10] Plazinski, W. and Rudzinski, W. Kinetics of adsorption at solid/solution interfaces controlled by intraparticle diffusion: a theoretical analysis. *The Journal of Physical Chemistry C*, 113:12495-12501, 2009.

- [11] Dada, A. O., Olalekan, A. P., Olatunya, A. M. and Dada, O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. *IOSR Journal of Applied Chemistry*, 3:38-45, 2012.
- [12] Ayawei, N., Ebelegi, A. N. and Wankasi, D. Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry*, 2017, 2017.
- [13] Cantu, Y., Remes, A., Reyna, A., Martinez, D., Villarreal, J., Ramos, H., Trevino, S., Tamez, C., Martinez, A., Eubanks, T. and Parsons, J. G. Thermodynamics, kinetics, and activation energy studies of the sorption of chromium (III) and chromium (VI) to a Mn_3O_4 nanomaterial. *Chemical Engineering Journal*, 254:374-383, 2014.
- [14] Delley, B. From molecules to solids with the DMol³ approach. *The Journal of Chemical Physics*, 113:7756-7764, 2000.
- [15] Perdew, J. P., Burke, K. and Wang, Y. Erratum: Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Physical Review B*, 57:14999, 1998.
- [16] Appalakondaiah, S., Vaitheeswaran, G., Lebègue, S., Christensen N.E. and Svane, A. Effect of van der Waals interactions on the structural and elastic properties of black phosphorus. *Physical Review B*, 86:035105-035113, 2012.
- [17] Ortman, F., Bechstedt, F. and Schmidt, W.G. Semiempirical van der Waals correction to the density functional description of solids and molecular structures. *Physical Review B*, 73:205101-205110, 2006.
- [18] Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *Journal of Chemical Physics*, 92:508-517, 1990.
- [19] Zhou, J., Xiao, F., Wang, W. N. and Fan, K. N. Theoretical study of the interaction of nitric oxide with small neutral and charged silver clusters. *Journal of Molecular Structure: Theochem*, 818:51-55, 2007.