FeS Encapsulated Chitosan Graft Polyacrylamide Nanocomposite for the Uptake of Model Anionic Eosin Y from Water: Isotherm, Kinetics and Equilibrium Studies.

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Abstract

A novel bio-nanocomposite, FeS encapsulated chitosan grafted polyacrylamide, was successfully synthesized using a grafting technique that employs microwave irradiation. Employing FTIR, SEM, XRD, TEM and SAED analysis, the synthesized nanocomposites were characterized. Thermodynamic and kinetic studies were accomplished using the batch mode via the eosin yellow adsorption from aqueous solution using the nanocomposite. The adsorption process was tailored to the pseudo-second-order kinetic model and the Freundlich isotherm model. The enthalpy change, ΔH° (-12.243 kJ/mol), was an exothermic process. The Gibbs energy, ΔG° (from -5.492 kJ/mol.K to -5.078 kJ/mol.K for temperatures from 300 K to 318 K respectively) values were indications of a thermodynamically feasible reaction process which was spontaneous within the temperature domain. The change in entropy, ΔS° (-0.023 kJ/mol), showed reduced randomness during the adsorption process. The mean free energy of adsorption was 0.408 kJ/mol, which was an indication of physisorption. These results show the possible use of the graft copolymer as an adsorbent in water treatment.

1. Introduction

Water pollution due to the discharge of effluents from industries is of critical concern owing to its hazardous nature and threat it poses to humans and the environment. A major industry that contributes to the release of these effluents is the textile and dyeing industry. Textile and dyeing industries utilize a generous amount of water during manufacturing and employ toxic colorants such as dyes in the colouring of their final products. Consequently, they are considered one of the largest generators of contaminated wastewater [1–5]. Owing to the complexities of the aromatic structure of most dyes, it is an arduous task to remedy these pollutants since they are stable to light and heat and non-biodegradable [6]. Various remediation techniques which include chemical oxidation, electrocoagulation, coagulation, anaerobic and aerobic microbial degradation, membrane separation and adsorption have been explored extensively for the uptake of dyes from contaminated effluents [7, 8]. Conversely, adsorption has demonstrated to be a good and efficient means of treating dye effluents, because it gives off highly treated effluents. Several suitable low-cost adsorbents, namely peat, silica, bentonite, fly ash, wood shavings and maize cob [9] have been employed in wastewater treatments but these adsorbents generally have low removal rate thus large magnitudes are needed for the complete treatment of dye effluents [6]. Recently, attention has been concentrated on biomaterials for dye removal owing to their advantage over synthetic polymers. These biomaterials are biodegradable, low cost and easily available [10]. Another advantage is that they do not leave residues of the by-products and can easily be isolated after the adsorption process is completed [10–12]. Despite these advantages, biopolymer-based adsorbents have poor mechanical strength and water solubility as compared to synthetic polymers. It is, therefore, necessary to improve their strength and stability by modifying its properties by graft copolymerization and the incorporation of nanoparticles [13, 14]. Nanoparticle-based adsorbents have drawn significant attention because of unique properties such as very small size and high surface area to volume ratio [15, 16]. Integration of these nanoparticles inside the polymer matrix not only grows the

surface area but also provides additional properties for the attachment of dye molecules [17]. Graft copolymerization is the method in which one or more polymers are covalently bonded to the polymer backbone of another polymer [18].

Chitosan is known to be a bio-compatible, biodegradable, bio-inexhaustible, non-toxic polymer and the second most bounteous regular polysaccharide after cellulose known to mankind. It is obtained from the deacetylation of chitin which takes place in the exoskeleton of insects, crustacean shells, shrimps, prawns as well as the cell walls of fungi [19, 20]. Due to its amine and hydroxyl functional groups, it can attract the alkyl, acetyl, sulphonyl and carboxylic groups in dyes [21]. Acrylamide is a receptive composite utilized as a monomer for the amalgamation of polyacrylamide. Owing to its elevated-water retaining capacity, it has been utilized in wastewater treatment and drug delivery [22].

In this work, chitosan was modified by microwave-assisted grafting of polyacrylamide followed by the dispersion of FeS nanoparticles for the adsorption of Eosin yellow from aqueous solutions. Experimental adsorption isotherms, kinetics data, and thermodynamic properties were analysed using different adsorption models.

2. Materials And Methods

All chemicals used were of analytical grade and used without further treatment. Glycerol, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Na_2S , ethanol, eosin yellow (EY), chitosan, acrylamide, and acetic acid were obtained from Sigma Aldrich, Germany.

2.1. Synthesis of FeS nanoparticle

Hundred (100) ml of aqueous 0.5 M of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 2 ml of glycerol were added together with vigorous stirring under N_2 gas atmosphere. 100 ml of Na_2S aqueous solution under continuous stirring was added dropwise to the mixture until a colour change was observed from pale green to brick brown and finally to dark green. This was stirred for about 20 minutes and washed with deionized water and ethanol repeatedly. The final product was then dried in a hot air oven at 333 K overnight. Dried FeS was powdered and stored for further application.

2.2. Fabrication of FeS/chitosan graft poly(acrylamide) nanocomposite

Two (2) g of chitosan was dissolved in 100 ml 1% acetic acid and added dropwise to 50 ml acrylamide (0.1 M) solution with continuous stirring. An appropriate amount of FeS was added into the reaction mixture while stirring for about 45 minutes. The resulting mixture was set in a microwave reactor at 333 K for a period of 15–20 minutes at 15 psi pressure [22]. The product was washed copiously with deionized

water to take out any homopolymer that is created during the reaction. The final product was dried at 333 K in a hot air oven overnight, after which it was ground to powder and stored for future application.

2.3. Batch Experiments

Eosin yellow stock solution was prepared by dissolving 0.3 g in 1 L of deionized water. Using serial dilution, successive solutions required for the working solution were produced from the stock solution.

2.3.1. Adsorption Conditions

Using batch adsorption experiments, various parameters were determined by agitating a desired amount of the composite with the dye solutions (50 ml) of preferred pH and concentration on a mechanical shaker at 150 rpm agitation speed. The effect of contact time was varied between 10 to 90 minutes. For the effect of loading (adsorbent dose), 0.05 to 0.40 g of FeS/chitosan-g-poly(acrylamide) nanocomposite was agitated with 50 ml EY solution at constant concentration and temperature for 2 hours. Five (5) initial concentrations for EY ranging from 60 to 150 mg/L were utilized for studying the impact of EY concentration onto FeS/chitosan-g- poly(acrylamide) composite at 300 K. The influence of pH was varied between 2 to 10 using 0.1 M NaOH and 0.1 M HCl solutions. The impact of temperature was analyzed at several temperatures (300, 303, 308, 313, and 318 K) using 50 ml (100 mg L⁻¹) EY solutions in a MaxQ 8000 incubator stackable shaker. The residual EY concentrations in aqueous solutions were measured using a Shimadzu (UVmini-1240) UV-Vis spectrophotometer at an absorbance of 516 nm.

2.4. Theory

2.4.1. Removal Efficiency and Adsorption Capacity

The amount of dye adsorbed, Q_e or R.E were computed as follows:

$$R. E = \frac{C_o - C_f}{C_o} \times 100$$

1

where, C_o is initial EY concentration (mg L⁻¹), C_f is final EY concentration (mg L⁻¹)

and,

$$Q_e = \frac{C_o - C_f}{M} \times V$$

where, C_o is initial EY concentration (mg L^{-1}), C_f is final EY concentration (mg L^{-1}), M is mass of FeS/Chitosan-g-polyacrylamide (g)

V = volume of the EY solution (L)

2.4.2. Adsorption Isotherms

Adsorption isotherms portray the behaviour of the interaction between the adsorbent and the adsorbate molecules at equilibrium. The data obtained was tested using the Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm models. These isotherm models can be used to illustrate the equilibrium characteristics of adsorption.

The Langmuir isotherm assumes that there is a homogeneous dispersion of active adsorption sites on the adsorbent surface which absorbs a single layer adsorbate molecule with no interaction between the adsorbed molecules. The Langmuir isotherm equation is described by the equation [23];

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

3

where C_e (mg L^{-1}) is the liquid phase concentration at equilibrium and Q_e (mg g^{-1}) is the mass of the dye concentration absorbed per unit mass. A graph of $1/Q_e$ versus $1/C_e$ was plotted.

The Freundlich model assumes that with an increment in adsorbate concentration, the concentration of the adsorbate on the adsorbent surface also builds, corresponding to exponential decreases in adsorption energy after all the adsorption centers on the adsorbent are occupied. The expression for this model is [24];

$$\text{Log} Q_e = \frac{1}{n} \log C_e + \log K_F$$

4

where Q_e is the quantity of EY uptake per unit mass (mg/g), C_e is the equilibrium concentration of EY (mg L^{-1}) and K_F ($\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$) and $1/n$ are constants denoting the adsorbent capacity and the heterogeneity factor, respectively. The value of $1/n$ must be between zero and unity for favourable adsorption.

The Dubinin-Radushkevich isotherm describes whether the adsorption was physical or chemical. This is described by the equation [25–27];

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$$q_e = \ln q_{DR} - \beta \epsilon^2$$

where q_m (mg g^{-1}) is the Dubinin-Radushkevich maximum monolayer adsorption capacity, β ($\text{mol}^2 \text{J}^{-2}$) is activity coefficient associated to mean adsorption energy, and ϵ is the Polanyi potential which can be computed using the relationship

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

where R ($8.314 \text{ J mol}^{-1} \text{ K}$) is the gas constant, T (K) is temperature and C_e (mg L^{-1}) is the concentration of adsorbate at equilibrium.

2.5. Characterization

The morphology of the nanocomposite and the grafted copolymer were obtained using scanning electron microscope (SEM) and transmission electron microscope (TEM). Selective area electron diffraction (SAED) analysis was obtained from the TEM. X-ray diffraction (XRD) analysis was used for the identification of the crystal structure of the materials. Fourier transform infra-red spectroscopy (FTIR) was used to determine the functional groups and the chemical bonds present in the materials.

3. Results And Discussion

3.1. FTIR Analysis

The FTIR spectra of FeS NP and FeS/chitosan-g-poly(acrylamide) nanocomposite are shown in Fig. 1 (A, B). Figure 1A showed a wide peak at 3332 cm^{-1} attributed to O-H vibrations from water molecules absorbed by the sample. Peaks at 1632 cm^{-1} and 621 cm^{-1} were as a result of S-S vibrational stretch from the FeS nanoparticle [28]. A peak at 1133 cm^{-1} was characteristic of the S-O stretching vibration. In the fingerprint region, vibration bands corresponding to Fe-S stretch were observed below 500 cm^{-1} [29]. The FTIR of the grafted nanocomposite (Fig. 1B) showed a broad absorption band at 3188 cm^{-1} which was due to N-H vibrations of amide groups and O-H stretching of chitosan coinciding. A band at 1543 cm^{-1} was ascribed to the (C=O) vibrations of secondary amide [30, 31]. A band at 1401 cm^{-1} was due to C-N vibrational stretch which was an indication of the grafting between chitosan and polyacrylamide [30]. Peaks found below 500 cm^{-1} were as a result of Fe-S stretching mode [22, 29]. The shift in peak positions of Fe-S bands indicated the interaction of the copolymer with the nanocomposite.

3.2. XRD Analysis

Fig 2 shows the XRD patterns of the as-synthesized FeS NP and FeS/chitosan-g-poly(acrylamide) nanocomposite. The peak positions (2θ values) at 17.56° , 28.83° and 40.75° corresponded to reflections from the (001), (101) and (111) planes of the tetragonal FeS phase (JCPDS: 86-0389) [29]. The grafted nanocomposite showed lower intensity in the peaks as compared to the FeS NP. This may be due to the interaction of the polymers (chitosan and polyacrylamide) with the nanoparticle and the less crystalline nature of the nanocomposite, compared to the nanoparticle [31]. From the Sherrer equation, the crystallite size of the FeS nanoparticle was found to be 6.2 nm.

3.3. SEM and TEM analysis

(Fig. 3A, B) shows the SEM and TEM micrographs of the as-synthesized FeS nanoparticle. The as-synthesized FeS nanoparticles were seen to be agglomerated and spherical or globular shaped. FeS NP synthesized through conventional methods, tend to agglomerate rapidly to macroparticles due to the interparticle van der Waals interaction [32]. Similar spherical shaped results were reported by other researchers [28, 33–35]. Figure 3C, D shows SEM image of FeS/chitosan-g-poly(acrylamide) nanocomposite and the SAED pattern of FeS NP obtained from the TEM microscope respectively. The SEM of the graft nanocomposite revealed that FeS NP was coated by the copolymer. The flake-like appearance was due to the grafting of FeS and polymers (chitosan and acrylamide) [31]. Though not all of the chitosan and acrylamide were fully grafted.

The SAED pattern of FeS (Fig. 3D) showed small spots forming rings ascribed to the Bragg reflections from the individual crystallite of the FeS nanoparticle indicating polycrystalline nature of the particles [36].

3.4. Adsorption Removal Experiments

3.4.1. Effect of EY concentration, FeS/chitosan-g-poly(acrylamide) dosage and contact time

From the graph (Fig. 4A), the removal efficiency decreased from 92.32–86.56% with an increase in EY concentration. However, the amount of dye adsorbed per unit mass of the adsorbent increased from 55.39 mg g^{-1} to 129.84 mg g^{-1} with an increase in EY concentration. The decrease in R.E may be due to the fewer number of available surface-active sites as the concentration increased. The increase in Q_e may be ascribed to a huge driving force of the EY particles. At lower concentrations, fewer adsorbate particles are attached to the surface of the FeS/chitosan-g-poly(acrylamide) nanocomposite but as the concentration increased, the mass transfer driving force towards the adsorbent surface increased.

Fig 4B shows the effect of adsorbent dose on the adsorption of EY onto FeS/chitosan-g-poly(acrylamide) nanocomposite by varying the dosage in 50 ml of the dye solution. The removal efficiency increased from 66.11% to 92.32% up to 0.15 g dose after which there was a gradual plateau in

a decreasing manner. The initial increase may be ascribed to the availability of adsorption sites and the plateau and eventual decrease may be a result of saturation of the adsorption sites. However, Q_e reduced from 78.16 mg g^{-1} to 11.48 mg g^{-1} with an increase in FeS/chitosan-g- poly(acrylamide) dose. This may be as a result of the adsorbent surface sites available to EY overlapping. However, any additional increase in FeS/chitosan-g- poly(acrylamide) dosage had little effect on the adsorption.

The overall trend for both R.E and Q_e was the same in Fig. 4C. There was a rapid rise in adsorption between the first 10 to 30 minutes after which there was a gradual rise. The rapid rise in the first 30 minutes may be due to the availability of more vacant adsorption sites.

3.4.2. Effect of Temperature and pH

The decrease in Q_e and R.E (Fig. 5A) with rising temperature indicate that the adsorption was an exothermic process. This may be due to a decrease in adsorptive forces between the adsorbate and the adsorbent as the temperature increased.

The amount of dye uptake per unit mass and removal efficiency of EY were strongly affected by the pH of the wastewater as shown in Fig. 5B. Q_e and R.E increased gradually. This may suggest that there was a higher affinity between the adsorbate and the nanocomposite at higher pH.

3.5 Adsorption Isotherms

To be able to efficiently utilize the adsorption system for practical applications, the Langmuir, Freundlich and the Dubinin-Radushkevich isotherms were employed in this work.

Figure 6 below shows the isotherm equilibrium data points for adsorption of EY onto FeS/chitosan-g- poly(acrylamide) nanocomposite.

From the graphs, the R^2 value of the Langmuir isotherm was 0.9591, Freundlich isotherm was 0.9657 and that of Dubinin-Radushkevich was 0.8243. It can be concluded that Freundlich isotherm fitted the system since the R^2 value was high.

The mean free energy of adsorption, E , was computed to be $0.408 \text{ kJ mol}^{-1}$ which was within the range of $0 < E < 8 \text{ kJ mol}^{-1}$ thus the adsorption was physical.

3.6. Adsorption Kinetics and Thermodynamic studies

To ascertain which kinetic order explains the adsorption of Eosin yellow onto FeS – chitosan-g- acrylamide composite, the contact time studies were evaluated using the pseudo-first order and the pseudo-second-order kinetics. The best fit results were obtained in the pseudo-second-order model with

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an R^2 value (0.9997) closer to unity as compared to the pseudo-first order R^2 value of 0.9673. Hence, it was established that the adsorption followed a pseudo-second-order process. A similar trend on the adsorption of Eosin Y was also reported [6, 37].

Table 1 below summarizes the thermodynamic studies of the adsorption process

Table 1
Thermodynamic parameters for EY adsorption onto FeS/chitosan-g-poly(acrylamide) nanocomposite

$\Delta H^\circ(\text{kJ mol}^{-1})$	$\Delta S^\circ(\text{kJ mol}^{-1})$	$\Delta G^\circ(\text{kJ mol}^{-1}.\text{K})$				
		300 K	303 K	308 K	313 K	318 K
-12.243	-0.023	-5.492	-5.252	-5.152	-5.005	-5.078

The negative ΔH° value indicated an exothermic process which correlates to the adsorption studies on the impact of temperature on the adsorption process. The negative value of ΔS° showed reduced randomness during the adsorption process. It also suggests that there was no substantial change going taking place in the internal structures of FeS/chitosan-g- poly(acrylamide) composite during the adsorption process [38]. The negative values of ΔG° suggested the spontaneity of the adsorption process.

4. Conclusion

FeS and FeS/chitosan-g-acrylamide nanomaterials were successfully synthesized by co-precipitation and microwave-assisted grafting respectively. The XRD spectra confirmed the tetragonal phase of FeS and particle size within the nanometer range. The FTIR confirmed the formation of FeS and its associated nanocomposite. SEM and TEM confirmed the morphology of the nanoparticle as well as the grafting of the polymers (chitosan and acrylamide). The SAED pattern indicated the polycrystalline nature of the nanoparticle. Batch adsorption studies revealed the dependency of the nanomaterial on adsorbent dosage, pH, temperature, contact time and adsorbate concentration. The Freundlich isotherm model fitted the adsorption process. This is an indication of heterogeneous adsorption. The thermodynamic parameters according to the ΔG° showed a spontaneous and thermodynamically stable process, the ΔS° indicated a reduced disorderliness in the adsorption process and the ΔH° depicted an exothermic adsorption process. The FeS/chitosan-g-acrylamide, therefore, showed potential use as an adsorbent for the removal of organic dyes (Eosin Y) from wastewater.

Declarations

Availability of data and materials

Not applicable

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Competing interests

The authors declare they have no competing interests.

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Authors' contributions

Eric S. Agorku: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - Review & Editing, Visualization, Supervision, Project administration.

Bernice Y. Danu: Methodology, Validation, Investigation, Formal analysis, Writing - Original Draft, Visualization

Francis K. Ampong: Writing - Review & Editing, Supervision.

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Figures

Figure 1

FTIR spectra of FeS NP (A) and FeS/chitosan-g-poly(acrylamide) nanocomposite (B).

Figure 2

XRD patterns of FeS NP (A) and FeS/chitosan-g-poly(acrylamide) nanocomposite (B).

Figure 3

SEM image of FeS NP (A), TEM image of FeS NP (B), SEM image of FeS/chitosan-g-poly(acrylamide) nanocomposite (C), SAED pattern of FeS NP (D).

Figure 4

Effect of concentration (A), dosage (B) and contact time (C) on EY adsorption onto FeS/chitosan-g-poly(acrylamide) nanocomposite. Conditions: (A. temperature: 300 K; time: 120 minutes; dose; 0.05 g/50 ml) (B. temperature: 300 K; Time: 120 minutes; concentration: 100 mg L⁻¹) (C. concentration: 100 mg L⁻¹; dose; 0.05 g/50 ml; temperature: 300 K).

Figure 5

Effect of temperature (A) and pH (B) on EY adsorption onto FeS/chitosan-g-poly(acrylamide) nanocomposite. Conditions: (A. concentration: 100 mg L⁻¹; time: 30 minutes; dose; 0.05 g/50 ml) (B. temperature: 300 K; Time: 120 minutes; concentration: 100 mg L⁻¹).

Figure 6

Langmuir (A), Freundlich (B) and Dubinin-Radushkevich (C) plots of EY adsorption onto FeS/chitosan-g-poly(acrylamide) nanocomposite.