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Adsorption of Rhodamine-B on Functionalized Hydroxyapatite-Chitosan-Titanium Dioxide Nanoparticles

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ABSTRACT

The research connotes the beneficial use of decomposable Functionalized Hydroxyapatite-Chitosan-Titanium Dioxide Nanoparticles (FHC-TiO_2NPs). Hydroxyapatite produced from the Periwinkle shell was functionalized with Chitosan and TiO_2NPs for uptake of Rhodamine B (Rh-B) from aqueous medium. The adsorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction Analysis (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDX). Reduced strengths of peaks, greater irregular cavities, and lesser particle diameters of functionalized biogenic materials confirmed functionalization. The adsorption efficiency was obtained at pH 9 (26.38 %), dosage 0.5 g (91.51 %), initial Rh-B concentrations 10 mg/l (95.23 %), contact time 10 min (2.82 mg/g), and temperature 303 K (52.29 %). The batch adsorption revealed that FHC-TiO_2NPs are capable and sustainable sorbent for eliminating Rh-B dye from aqueous medium due to its constant availability.

KEYWORDS: Adsorption, Rhodamine B, Biosorbent, Functionalization, Nanoparticles, Characterization.

1. INTRODUCTION

Rh-B is a glowing dye usually utilized in various scientific and industrialized applications. At the same time, nanoparticles (NPs) have added substantial care for their exclusive properties and potential applications across different fields.[1] Rh-B is frequently employed as a fluorescent probe to label biological samples, visualize cells and track molecular interactions in various experiments. Additionally, it finds applications in the textile, cosmetics, and food industries as a colorant.[2]

Hydroxyapatite is a crystalline substance that belongs to the apatite group of minerals and has a chemical formula of $Ca_5(PO_4)_3OH$.[3] This unique composition gives hydroxyapatite its exceptional biocompatibility and makes it an essential component of the skeletal structure. Hydroxyapatite forms elongated crystals that are similar in shape to needles, with a white to off-white color.[4] Hydroxyapatite nanoparticles are utilized in the development of advanced drug distribution systems and material engineering scaffolds.[5] Nanoparticles can be engineered to possess specific properties, making them valuable for targeted drug delivery, imaging, sensing, and enhancing material performance.[6]

Chitosan-titanium dioxide nanoparticles (CTNPs) are composite materials formed by combining chitosan, a biopolymer derived from crustacean shells, with TiO_2NPs.[7] Continued research and development in this field will likely unveil new opportunities for CTNPs in diverse industries, contributing to technological advancements and improved sustainability.[8] The aim of this research is to examine the batch adsorption performance of Rh-B on FHC-TiO_2NPs.

2. MATERIALS AND METHODS

2.1. Materials

Titanium dioxide (TiO_2), Hydrochloric (HCl), Sodium hydroxide (NaOH), Sodium chloride (NaCl), and Rh-B with molecular formula $C_{28}H_{31}N_2O_3Cl$ was bought from Sigma-Aldrich, Germany were all used to model dye wastewater by making a stock solution of 0.1 gl^{-1} Rh-B. The chemicals used in these studies were obtained from Sigma Aldrich. Fresh periwinkle shells were obtained from Oyingbo market, Lagos State. All reagents and chemicals used were of analytical grade.

2.2. Production of Hydroxyapatite from periwinkle shell.

The dried up periwinkle shell (PS) was calcined using an electronic furnace at 600 °C for 2 hrs. The calcined sample was crushed into granular form and sieved to a unit size of 2 mm (to allow higher compaction for improvement of adsorptive property), soaked with 0.26M Di-ammonium hydrogen phosphate solution (acts as a precursor for the formation hydroxyapatite) for 24 hrs. The liquid part was decanted and the sediment was wash away continually with distilled-deionized water and drained using a Buchner funnel and suction pump, this was then oven-dried at 105 °C for 2 hr to eliminate moisture content completely. Prepared PSHAP was reserved in a tight container and kept in a desiccator for further use.[9,10]

2.3. Preparation of Adsorbent and Characterization

The hydroxyapatite and chitosan as adsorbents for the adsorption process were functionalized using TiO_2NPs. 20 ml of TiO_2NPs was measured into a 100 mL beaker and 40 g of Hydroxyapatite and chitosan were weighed and added to it. The mixture is stirred thoroughly for some minutes. After the mixture was thoroughly stirred, it was placed inside the oven- and dried at 60^0C for hours.

Surface chemistry of hydroxyapatite and chitosan with TiO_2NPs was characterized by FTIR Model 500, Buck Scientific Inc.) in the range of 400– 4000/cm, SEM (Bruker-X Flash 6130, Carl Zeiss, EVO 18 Research, Germany) in the wavelength λ = 10 – 10m, EDX (JEOL JSM-6510LA, Japan).[11,12]

2.4. Preparation of Adsorbate Solution

The stock solution using 1000ml of the adsorbate was arranged by adding 0.2 g of Rh-B to 1000 ml of distilled water. Subsequently, 50 ppm was prepared from the stock solution.[11,12]

2.5. Adsorption Studies

The pH point of zero charges (pHpzc) was determined. A considered amount (0.25g) of hydroxyapatite-chitosan-TiO_2NPs was weighed and put into 50 ml of 0.1 M NaCl with a prearranged pH in a 250-ml conical flask. The pH of the resulting solution was modified between pH 1 and 12 with either 0.1 M NaOH or HCl. The conical flasks were enclosed and left for 24 hrs after which the last pH values were determined. The variance between the initial and final pH was calculated and plotted against the initial pH.[11,12,10]

Effect of pH was studied between pH 2 and 12 by adjusting Rh-B solution with 0.1 M HCl or 0.1 M NaOH, it was decanted and centrifuged at 3000 rpm for 15mins followed by the measurements of its absorbance spectrum using UV-Visible spectrophotometer operated at the range 190-900 nm.

The effect of dosage was investigated. Approximately 0.1 to 0.5 g of adsorbent (hydroxyapatite-chitosan-TiO_2NPs) was added to 50 ml of 50 mg/L Rh-B solution in a 250 ml conical flask respectively. The flasks were agitated at 300 rpm for 30 min in a thermostat-regulated water bath with a shaker (Uniscope water bath shaker) at 30℃, It was decanted and centrifuged at 3000rpm for 15min, followed by the measurements of its absorbance spectrum using UV-Visible spectrophotometer operated at the range 190-900 nm.[11,12,10]

The effect of initial concentration of Rh-B was investigated. Rh-B solution was diluted through serial dilution used to prepare the other five concentrations (10-50 mg/l). Exactly 1 g of hydroxyapatite-chitosan-TiO_2NPs was added to 100 ml of each solution and put inside the water bath shaker agitated at 150 rpm at an ambient temperature condition of 30 ℃. Then Rh-B solution solution was decanted and centrifuged at 3000 rpm for 15 min.

The effect of temperature was investigated. 0.25g of the adsorbents was added to 50 ml of 50mg/l Rh-B solution in a 250ml conical flask, the mixture was put inside the shaker and then agitated at 150 rpm and 30^0C. The samples were taken after 30 mins of agitation. The influence of solution temperature on the Rh-B sorption process was observed at different temperatures: 35, 40, 45, 50, and 55°C respectively. This was done by adjusting the temperature regulator of the water bath shaker.[11,12,13]

The effect of contact time on Rh-B concentrations was investigated. 5g of hydroxyapatite-chitosan-titanium dioxide nanoparticles were weighed into 500 ml of Rh-B solutions separately, and 100 mins were used for the contact time. The water bath was adjusted to 30^0C, 5ml was taken from each of the solutions after 10-minute centrifuges, and a UV spectrometer was used to determine the

absorbance.[11,12,13] Percentage removal and quantity adsorbed at a given time t were calculated using the following equations:

$\% Removal = (Co - C_f / Co) \times 100$ ..... (1)

$qt = (Co - C_t)\, V/M$ ..... (2)

Where qt is the amount of Rh-B adsorbed per unit mass of adsorbent (mg/g)
Co is the initial Rh-B concentration (mg/l), C_f is the final Rh-B concentration (mg/l). , Ct is the residual concentration at time t, V is the volume of Rh-B solution (l) and M mass of adsorbent (g).

3. RESULTS AND DISCUSSION

The FTIR study was used to define the functional groups existing in the FHC-TiO_2NPs (figure 3a-c). The occurrence of peak at 3433.41 cm^{-1} was owing to the stretching vibration of the N-H bond in the chitosan. The peaks at 1743.88 and 1637.95 cm^{-1} are owed to the stretching vibrations of the C=O bond in the amine and amide groups of the chitosan, respectively. The peak at 1387.56 cm^{-1} was as a result of the bending vibration of the C-H bond in the amine group. The peaks at 1006.80 and 875.55 cm^{-1} were owing to the stretching vibrations of the P-O bond in the hydroxyapatite confirms that the nanoparticles had been successfully functionalized with hydroxyapatite and chitosan.

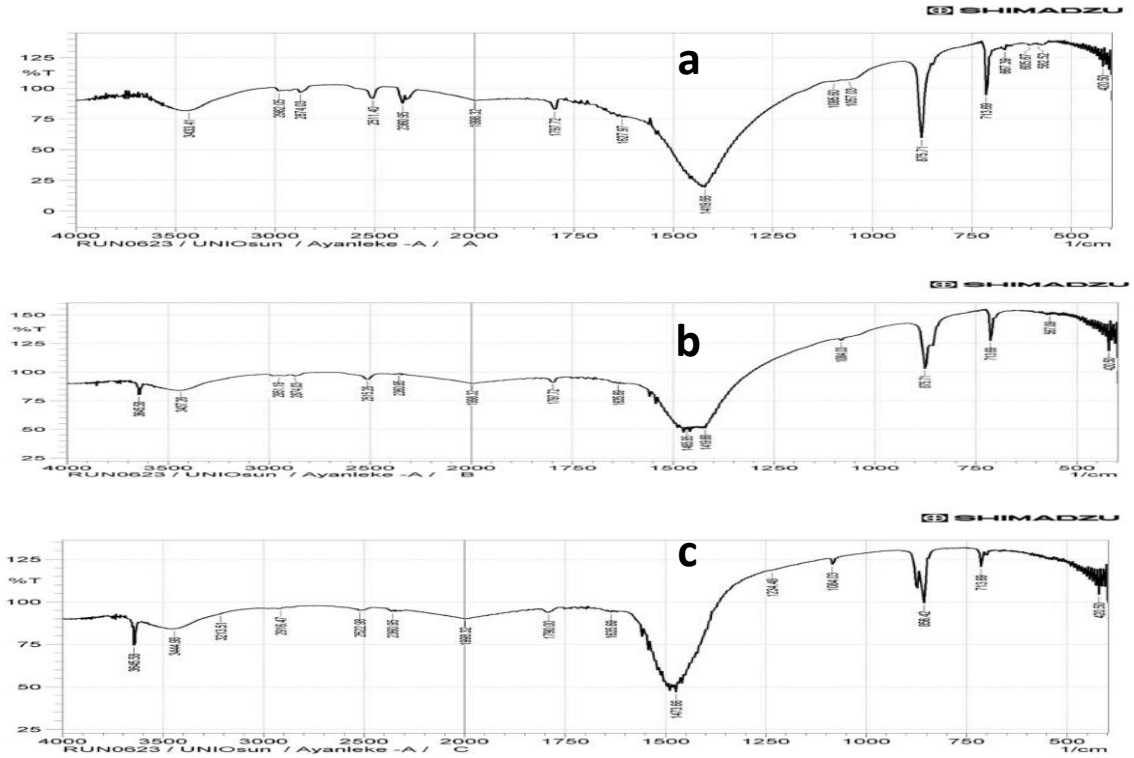

Figure 3a-c: FTIR spectra of (a) FHC-TiO_2NPs (b) Hydroxyapatite (c) Chitosan

The XRD pattern of the FHC-TiO_2NPs showed the characteristic peaks of both hydroxyapatite (HA) and chitosan (Figure 3d-f). This indicates that TiO_2NPs had been successfully functionalized with HA and chitosan.[11,12]

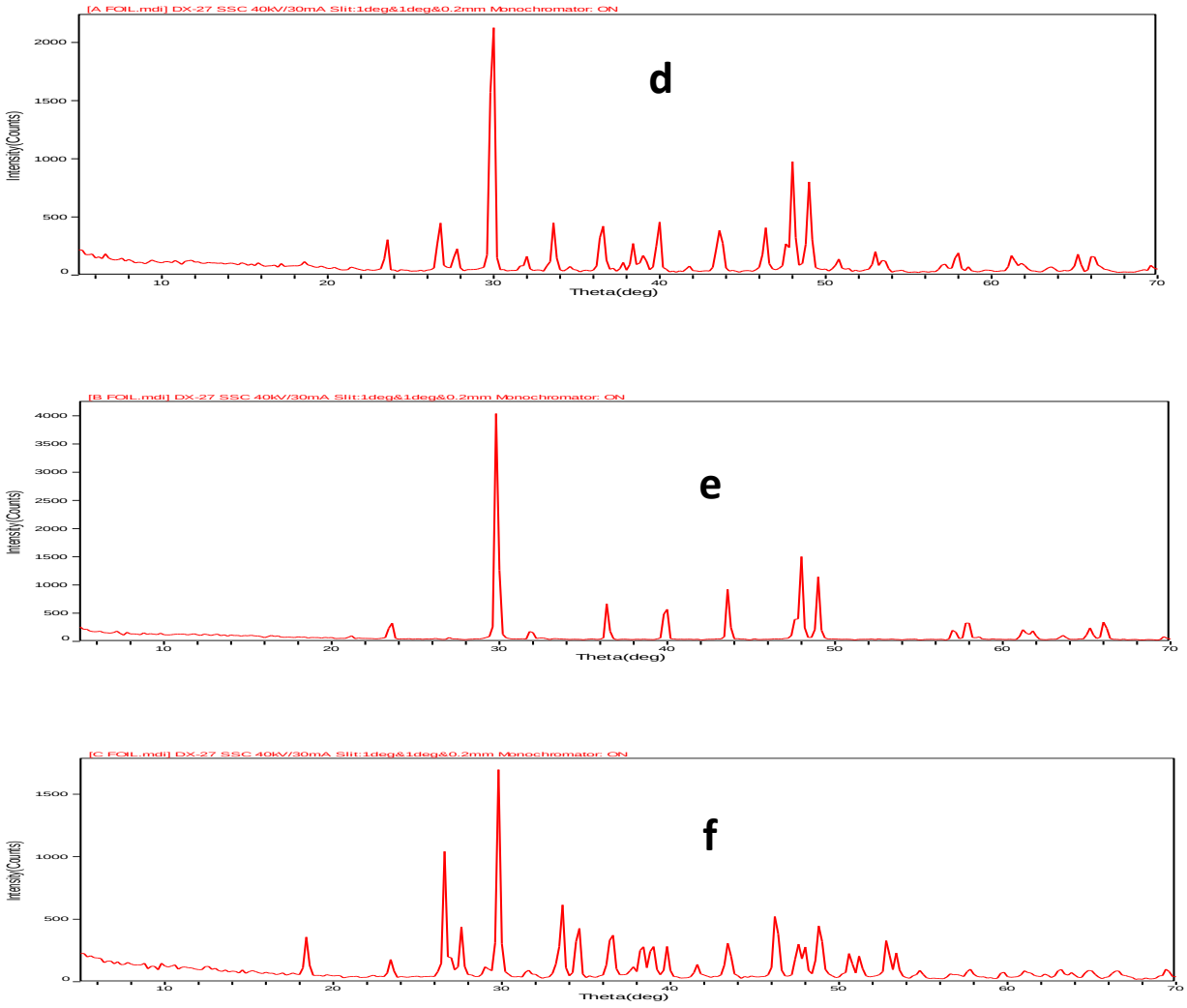

Figure 3d-f: XRD spectra of (d) FHC-TiO_2NPs (e) Hydroxyapatite (f) Chitosan

The SEM image (figure 3g) showed the surface of FHC-TiO_2NPs. The SEM image of the hydroxyapatite produced from the periwinkle shell (Figure 3h) showed that the particles are amorphous, meaning that they do not have a regular crystalline structure. The SEM image of chitosan produced from periwinkle shells (Figure 3i) showed that the molecules of chitosan are arranged in a hexagonal shape. The overall appearance of the SEM image is consistent with the expected properties of chitosan.[11,12]

Figure 3g: SEM image of FHC-TiO_2NPs

Figure 3h: SEM image of Hydroxyapatite

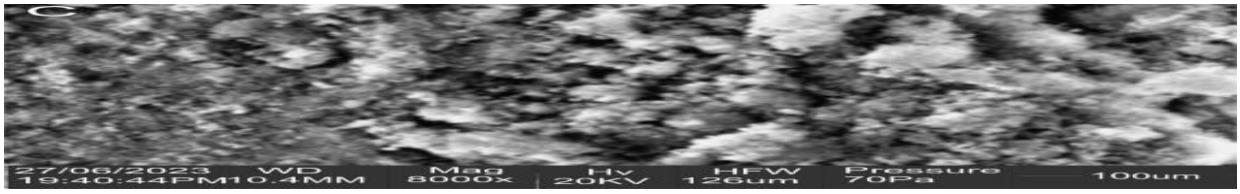

Figure 3i: SEM image of Chitosan

The EDX results showed FHC-TiO_2NPs were successfully functionalized (Fig. 3j). The major elements present are Calcium (60 %), Oxygen (20 %), Phosphorus (8 %), Potassium (4n %), Carbon (4 %), Manganese (2 %) and Sodium (1 %) (Azeez *et al*., 2022, 2024). EDX results (Fig. 3k) showed that hydroxyapatite produced from the periwinkle shell was made up of the following elements: Silicon (60 %), Phosphorus (13 %), Calcium (12 %), Iron (3 %), and Sodium (2 %). The EDX result of Chitosan produced from periwinkle shells (Fig. 3l) showed that the chitosan has a high concentration of calcium and magnesium. This is consistent with the fact that periwinkle shells are a good source of these minerals.[11,12]

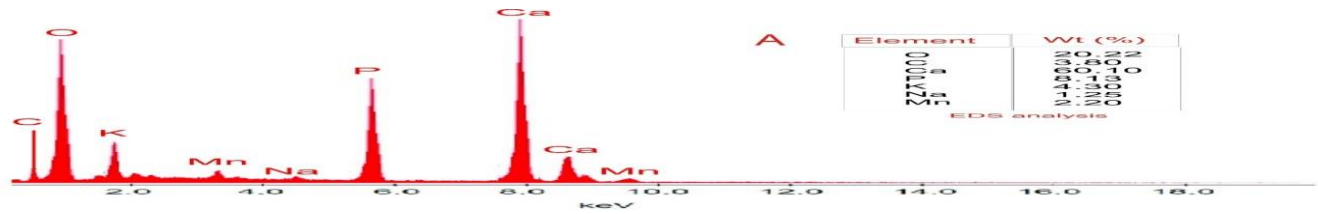

Figure 3j: EDX of FHC-TiO_2NPs

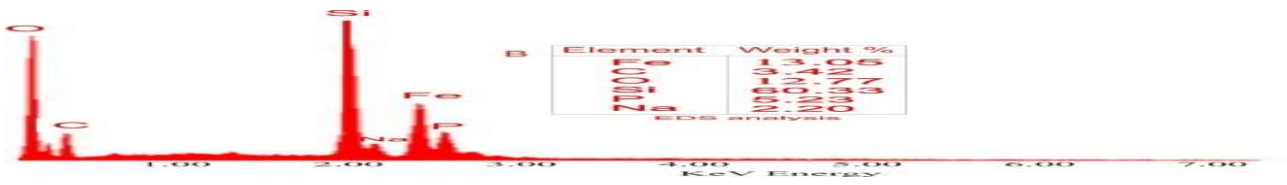

Figure 3k: EDX of Hydroxyapatite

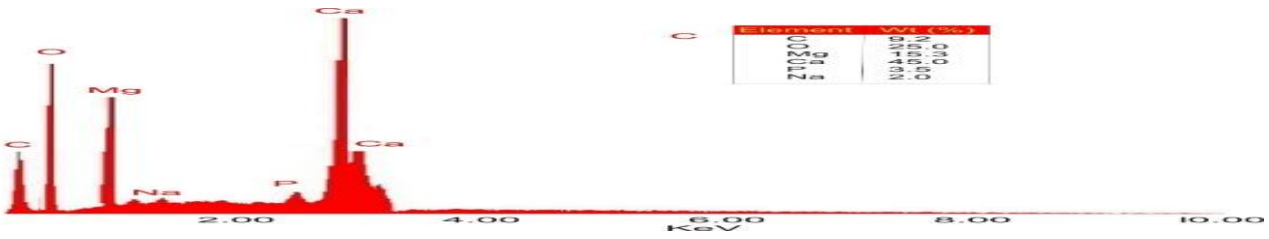

Figure 3l: EDX of Chitosan

3.1. Adsorption Studies

pHpzc for FHC-TiO_2NPs occurred at 9.0 suggesting maximum adsorption of Rh-B will be effective above this pH value (fig.3.1a).

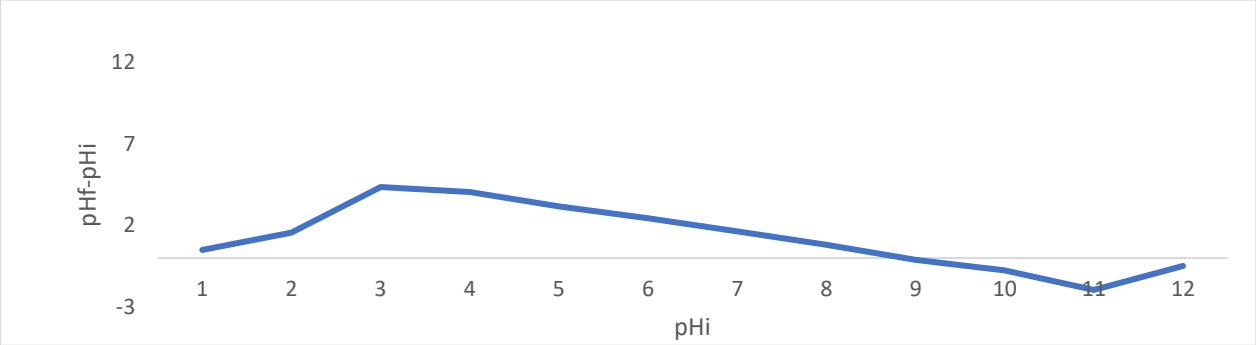

Fig. 3.1a: pH point of zero charge

The relationship between the initial pH value (2-12) and the percentage of Rh-B removal onto FHC-TiO_2NPs showed an irregular pattern. Therefore, the maximum adsorption percentage removal efficiency (26.38 %) was attained at a pH of 9 (fig.3.1b).

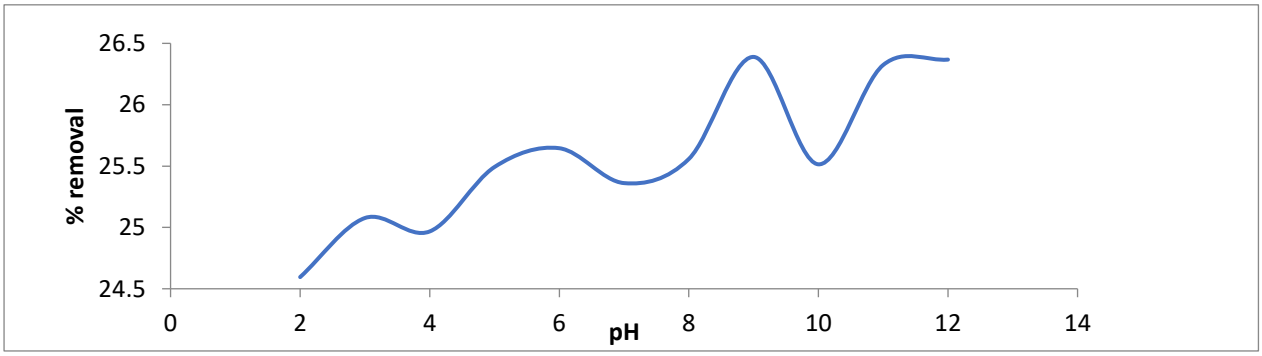

Fig.3.1b: Effect of pH on the adsorption of Rh-B

The outcome of the upshot of the adsorbent dosage on the percentage Rh-B removal efficiency (91.51 %) from aqueous medium was attained at 0.5 g. The percentage removal with an upsurge in adsorbent prescription from 0.1 to 0.5g for FHC-TiO_2NPs (fig.3.1c). This trend might be connected to a rise in the adsorbent surface area and accessibility of more vital sites on the surface of FHC-TiO_2NPs. The outcome of the upshot of Rh-B on the percentage removal of the Rh-B on FHC-TiO_2NPs.

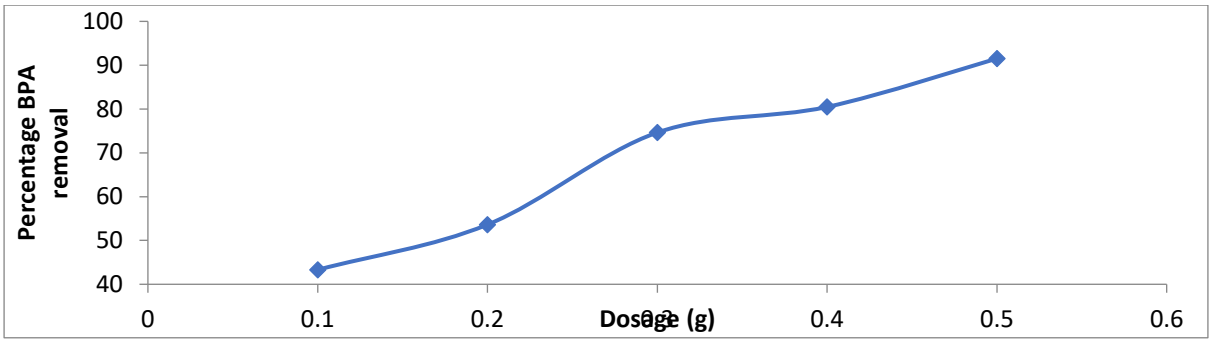

Fig.3.1c: Effect of adsorbent dosage

The percentage removal of Rh-B reduces with an upsurge in the initial Rh-B concentration, the extreme removal effectiveness obtained from Rh-B was 95% at 10 mg/l (fig.3.1d). The decrease in the removal efficiency of Rh-B as the initial increase suggested that the absorbent sites are filled up early in the process and maximum adsorption was achieved.[11,12,10]

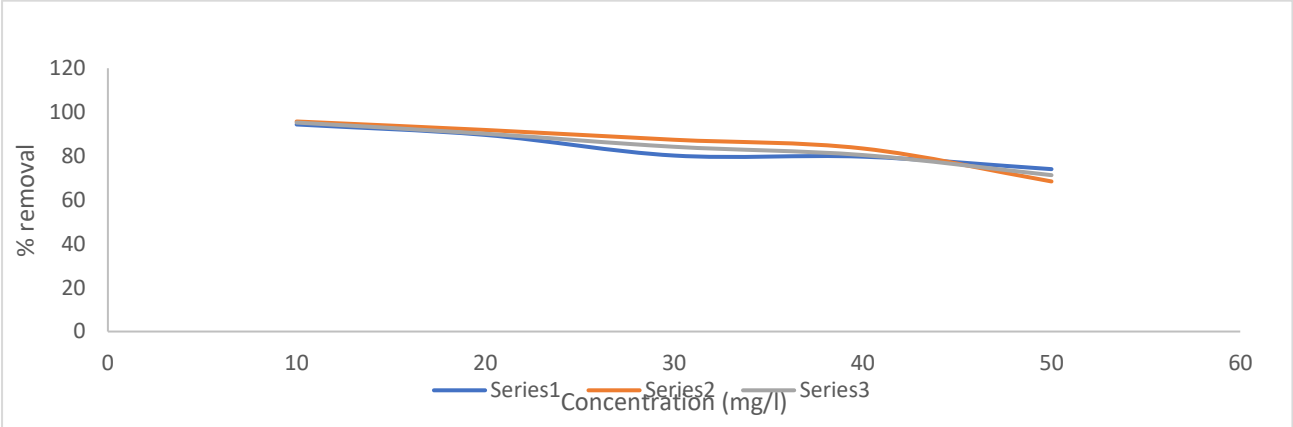

Fig 3.1d: Effect of initial conc. Rh-B

The outcome of the upshot of contact time on Rh-B uptake onto FHC-TiO_2NPs was presented (Fig 3.1e). The amount of Rh-B adsorbed at time t (qt) was initially rapid within the first 10 minutes and slowed steadily before attaining equilibrium at 60 minutes (2.82 mg/g). The initial upsurge in quantity adsorbed is attributed to the obtainable abundant surface reactive sites which were engaged as the adsorption proceeded.

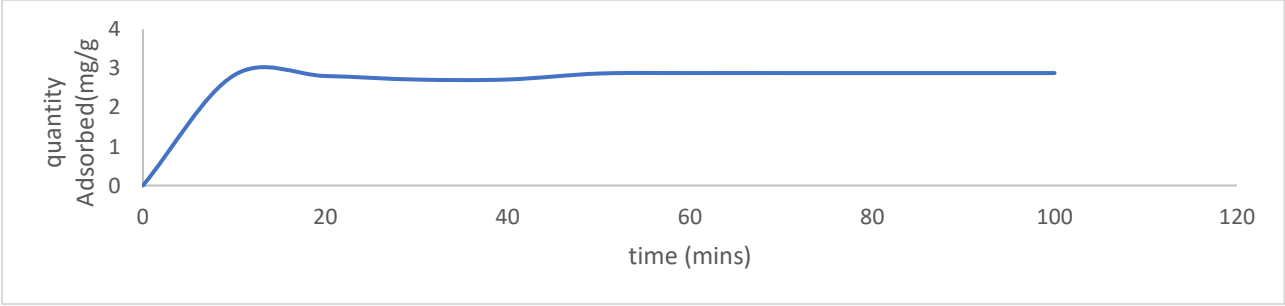

Fig.3.1e: Effect of contact time

The upshot of temperature on percentage Rh-B removal efficiency onto FHC-TiO_2NPs was 52.29 % at 303 K (Fig.3.1f). Removal efficiency of Rh-B decreased with a rise in temperature for the adsorbent used. The binding forces between the adsorbent and the adsorbate reduces with an upsurge in the temperature and subsequently upshot in reduced percentage removal.[11,12,10]

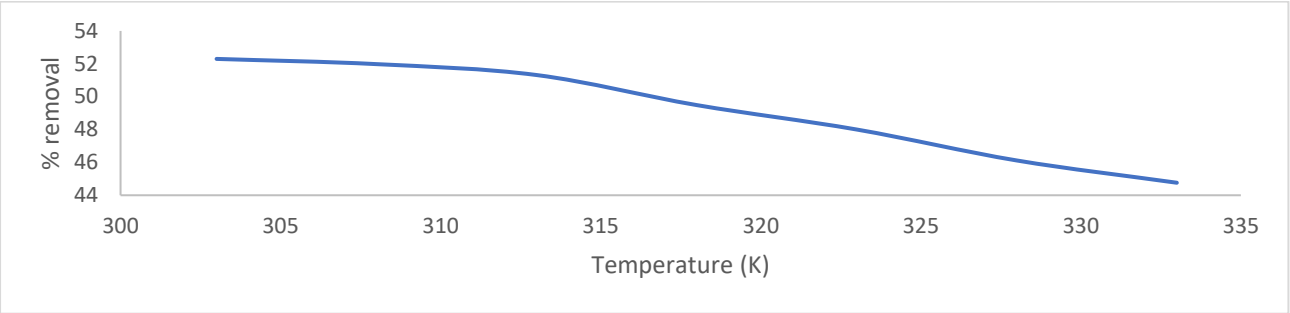

Fig 3.1f: Effect of temperature

4. CONCLUSION

This study showed that pH, dosage, initial concentration, temperature, and contact time affected surface functionalized hydroxyapatite-chitosan-TiO_2NPs, which improved its adsorptive performance and reusability. The uptake of Rh-B dye onto FHC-TiO_2NPs\ was greatly reliant on operational parameters. It also revealed that FHC-TiO_2NPs material is a capable and sustainable sorbent for eliminating Rh-B dye from aqueous solution due to its constant accessibility and reusability.

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