

Sustainable Synthesis of Ananas Comosus (Pineapple Peel)-Zinc Nanoparticles (PA-Zn Nps) for Congo Red Dye Remediation

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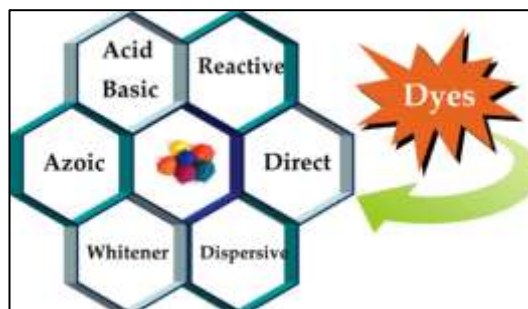
Abstract

The green synthesise route emphasizes reduction in NP production and use of Nanotechnology from the disposals of harmful pollutants available in the effluents, and liberation these generated NPs for minimum environment toxicity. The extract from Ananas Comosus (Pineapple Peel) was selected for the present investigation because it possesses good adsorbent properties and contains flavonoids and steroids which are helpful as antioxidants and also shows reducing properties leading to the formation of PA-Zn Nps. The SEM-EDX, XRD, and FTIR methods are employed to study the behaviour of Ananas Comosus (Pineapple Peel)-Zinc Nanoparticles. The experiment is based on the adsorption methodology to eliminate Congo Red Dye. Different conditions including Agitation Time, amount of sorbent used, pH of Solution, Starting dye Concentration and Temperature were reported and optimized. Freundlich and Langmuir Isotherms models proved to be the greatest fitting models for the experimented adsorptive data of dye with PA-Zn Nps.

Keywords: (Ananas Comosus) Pineapple Peel Extract, Green Synthesis, Nanotechnology, Adsorption Isotherms, Experimental Parameters, Kinetics.

1. INTRODUCTION

Organic substances called dyes are used to color materials such as leather, plastic, paper, and textiles. Chromophoric materials called dyes work with substrates to absorb particular light wavelengths, giving them color [1]. Dyes can adhere to fabrics and are soluble and colorfast. Additionally, they are sensitive to even minute amounts of metal ions. There are used in textiles, printing, cosmetics, and food are just a few of the industries that use dyes.



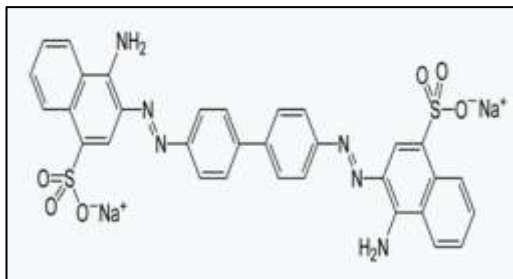
Dyes can be categorized according to their chromophore, application technique, and source (natural vs. synthetic) [2,3]. Plants or chemicals can be used to make dyes. Anaerobic breakdown of the dye solution might occasionally result in the formation of possibly cancer-causing substances that enter the food chain [4]. Furthermore, wastewaters with a lot of color can prevent sunshine and oxygen from penetrating, which is necessary for many aquatic life forms to survive.

For the wet processing of textiles, textile manufacturers use large amounts of chemicals and water. These chemicals are used for desizing, scouring, bleaching, dyeing, printing, and finishing. They range from inorganic compounds and elements to polymers and organic materials [5,6]. The Colour Index contains a list of over 8,000 chemical products related to the dyeing process, including various structural types of dyes, including acidic, reactive, basic (such as methylene blue, crystal violet, and safranin), disperse, azo, diazo, anthraquinone-based, and metal-complex dyes. In chemical engineering processes, adsorption is one of the unit activities used to separate contaminants from industrial wastewater. Pineapple peel extract is used in this study to synthesize doped zinc nanoparticles in an environmentally friendly manner [7]. The effects of agitation period, aqueous solution pH, adsorbent dosage, starting dye concentration in aqueous solution, and aqueous solution temperature are all examined in this study. The adsorption rate, adsorption capacity, and feasibility have been determined by the

study of kinetics, isotherms, and thermodynamics. The experimental data for adsorption of Congo Red dye from aqueous solution was acquired.

1.1 Congo Red Dye-

The sodium salt of 3,3'-[[1,1'-biphenyl]-4,4'-diyl]bis(4-aminonaphthalene-1-sulfonic acid) is an organic chemical known as Congo red. It's an azo dye. Congo red is more soluble in organic solvents and produces a crimson colloidal solution when dissolved in water. Congo red is still used for histological staining, but its application in the textile industry has long since been discontinued due to its carcinogenic qualities.



Chemical Formula: $C_{32}H_{22}N_6Na_2O_6S_2$

Molar Mass: 696.66 g/mol

Appearance: Red-brown powder

Solubility: Soluble in water and ethanol

pH Indicator Range: Changes from red (pH > 5.2) to blue (pH < 3.0).

Congo red is used to stain amyloid proteins in tissue samples, especially when identifying disorders such as amyloidosis. Under polarized light, Congo red-stained amyloid deposits show a distinctive apple-green birefringence, used as a pH indicator; changing color depending on the pH of the solution and is also used to stain certain bacteria and examine biofilms or structural components. Historically used to color fabrics, however its use in this industry has decreased due to safety concerns. Although having these many uses, Congo red is considered poisonous and potentially carcinogenic, hence its use in some applications has been curtailed. Proper disposal is essential to prevent environmental contamination.

1.2 Ananas Comosus-

Pineapple is a tropical fruit native to South America. It is the third most significant tropical fruit produced worldwide. Pineapple peels are a byproduct of the pineapple fruit, which typically contains 60% edible meat and 35% peel. Pineapples are widely grown in tropical regions around the world, including India, China, Malaysia, South Africa, Costa Rica, Nigeria, the Philippines, and Thailand. The scientific name for pineapple peel is *Ananas comosus*.



Pineapple peel is a byproduct of the canning business, yet it has numerous possible uses such as an Ethnomedicine which is a Malaria herbal therapy including the use of pineapple peel. Pineapple peel powder can serve as a useful food element in crackers and can also be used as fermented gross to improve protein content and used for animal feed. Bromelain, a digestive and an anti-inflammatory enzyme found in pineapple stems, helps break down proteins into amino acids and thus reduces swelling and pain [8].

Pineapple peels can be utilized as adsorbents because they are inexpensive, abundant, and have a porous structure that allows them to effectively remove contaminants from water. These can be chemically processed to remove colors and acid-soluble oligosaccharides, creating a porous structure that effectively eliminates contaminants. Bacterial cellulose aerogels can be generated from pineapple peel waste through a fermentation method which can absorb cationic dyes like methylene blue, malachite green, rhodamine B and crystal violet [9]. These peels can

also be used in the manufacturing of peel extract doped chemical adsorbent produced via a chemical activation process which are very efficient in the removal of tints from wastewater.

1.3 Zinc Nanoparticles (Zn Nps)-

Zn nanoparticles are water-insoluble white powders with high chemical, electrical, and thermal stability. Zinc nanoparticles have many applications, including in the catalyst industry, gas sensors, solar cells, and medicine [10]. Zn nanoparticles are used as effective adsorbents because of their large surface, high sensitivity and non-toxicity making them an Environmental friendly option the removal of dye from waste water effluents.



These nanoparticles can remove a wide range of dyes, including Congo red, Ismate violet 2R, direct blue 106, malachite green, rhodamine B and acid fuchsin. The adsorption of colors by Zn NPs depends on pH and temperature. Adsorption occurs primarily by chemical precipitation, electrostatic attraction, and hydrogen bonding [11]. These can also be reused numerous times without substantial loss of adsorption capacity. Zn NPs have many unique properties, including: biodegradability, biocompatibility, cationic capacity, high stability, and redox properties.

2. MATERIALS AND METHODS

Pineapple Peels were gathered from local areas.

2.1 Chemicals Required: Zinc Sulphate (ZnSO_4), HCl, NaOH.

2.2 Glassware: 1 lit beaker, Measuring jar, Pipette, conical flasks etc.,

2.3 Equipments: pH meter, Mechanical stirrer, Spectrophotometer, Orbital Shaker and Glass Ware etc.

2.4 Estimation of Dyes:

2.4.1 Preparation of Congo Red Sample-

1g of Congo Red dye was diluted in 1000 ml distilled water to prepare the Congo Red sample with a concentration of 1000 ppm. It is further diluted to prepare desired concentrations of the dye sample.



Figure 1- Congo red dye (powder)



Figure 2- Congo red dye solution

2.5 Synthesis of (Ananas Comosus) Pineapple Peel-Zinc Nanoparticles (PA-Zn Nps):

2.5.1 Preparation of Pineapple Peel Extract-

Fresh pineapple peels had been collected. Now, the fresh peel extract was made individually using 200 grams of fresh pineapple peels gathered. Seize a 1000ml conical flask, fill it with 1000ml of deionized water, and add 200g of fresh peels. The mixture should be stirred at 80°C for 60 minutes using a magnetic stirrer, and then allowed to cool. After the combination reaches room temperature, it was extracted by straining the liquid with the aid of whatmann filter paper. The filtrate obtained is the prepared pineapple peel extract, which can be stored at 4°C and utilized within a week [12].



Figure 3- Preparation of Peel Extract

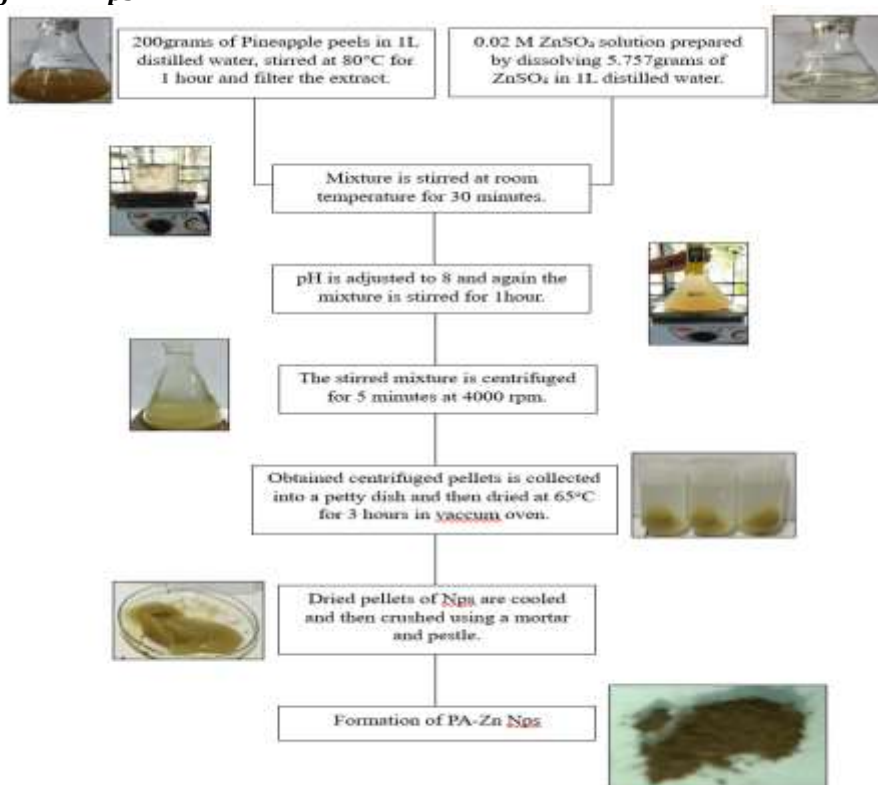
2.5.2 Preparation of Pineapple Peel-Zinc Nanoparticles (PA-Zn Nps)-

Pineapple Peel-Zinc nanoparticles (PA-Zn Nps) were made by combining freshly obtained pineapple peel extract and zinc sulphate solutions in the appropriate proportions. First, make a 0.02M ZnSO_4 solution by dissolving 5.751 grams of zinc sulphate granules in 1000 mL of water. Now, this prepared 0.02M ZnSO_4 is mixed with previously prepared fresh peel extract in a 5:2 ratio. The mixture should be stirred for 30 minutes using a mechanical stirrer at room temperature. After 30 minutes, the pH of the solution was measured and corrected by dropping some amount of 0.1 N NaOH solution upto the pH of the mixture reached to 8. The mixture was again stirred for 60 minutes. The stirred mixture is then centrifuged at a speed of 4000 rpm for 5 minutes [13]. Eventually, the obtained centrifuged pellets were collected into a petty dish and dried at a temperature of 65°C in a vacuum oven for about to a time period of 3 to 5 hours. Finally, the obtained dried pellets are crushed using a mortar and a pestle, therefore, the desired PA-Zn Nps are obtained and were stored carefully.



Figure 4- Preparation of PA-Zn Nps

2.5.3 Synthesis of PA-Zn Nps-



2.6 Characterization of PA-Zn Nps :

2.6.1 Screening of extract using SEM-

There is a visible distribution, with some particles being finer and others slightly larger, contributing to a **granular or particulate morphology**. The overall size range varies in the range of **50- 250 nm** which is consistent with a nanomaterial.

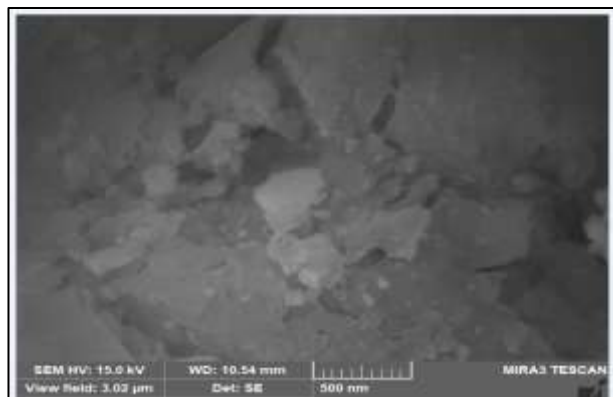


Figure 5- SEM image of PA-Zn Nps

2.6.2 X-Ray Diffraction (Analytics)-

Figure 6 presents the XRD pattern, with its maximum intensity centered at peak positions of 22.920, 24.940, 25.310, 26.520, and 32.9928. The pattern is indicative of an **amorphous, non-crystalline and a disordered material** as well as also indicates that it's a nanocrystalline material.

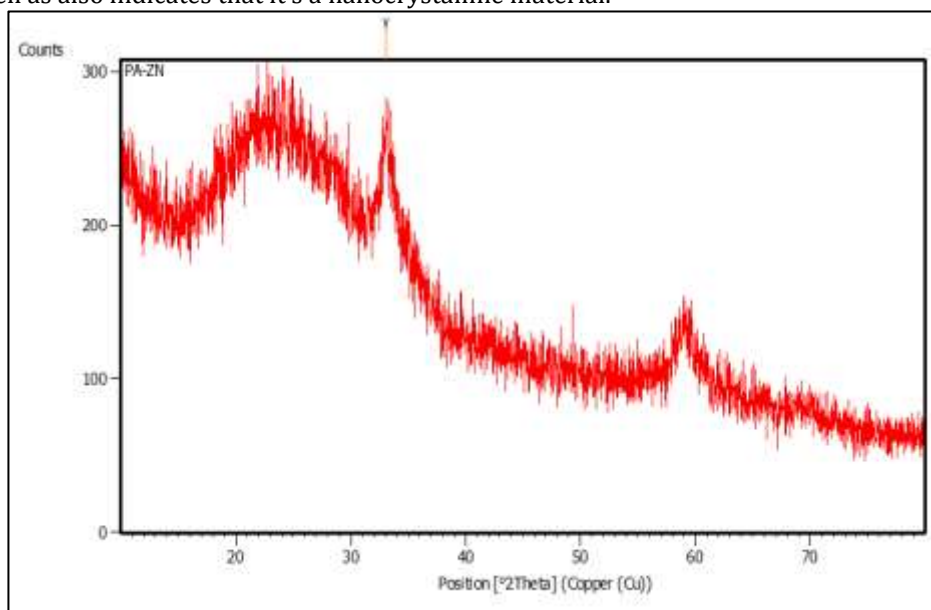


Figure 6- XRD image of PA-Zn Nps

3. RESULTS AND DISCUSSION

To maximize the percentage of adsorption of Congo Red Dye from the prepared dye sample, the variations of agitation time, sorbent quantity, solution pH, starting concentration of dye, and experimentation temperature were examined.

3.1 Charecterization of PA-Zn Nps :

3.1.1 Fourier Transform Infra-Red Spectroscopy (FTIR)-

FTIR spectrum of Pure PA-Zn Nps is given in Figure 7. The peaks at different points replicates different functional groups.

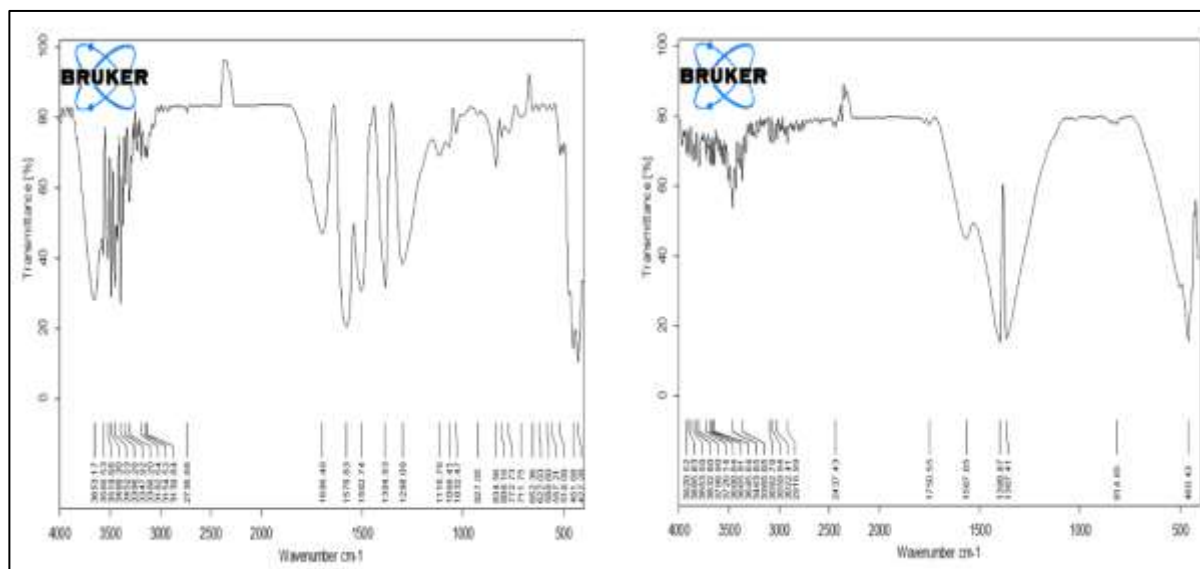
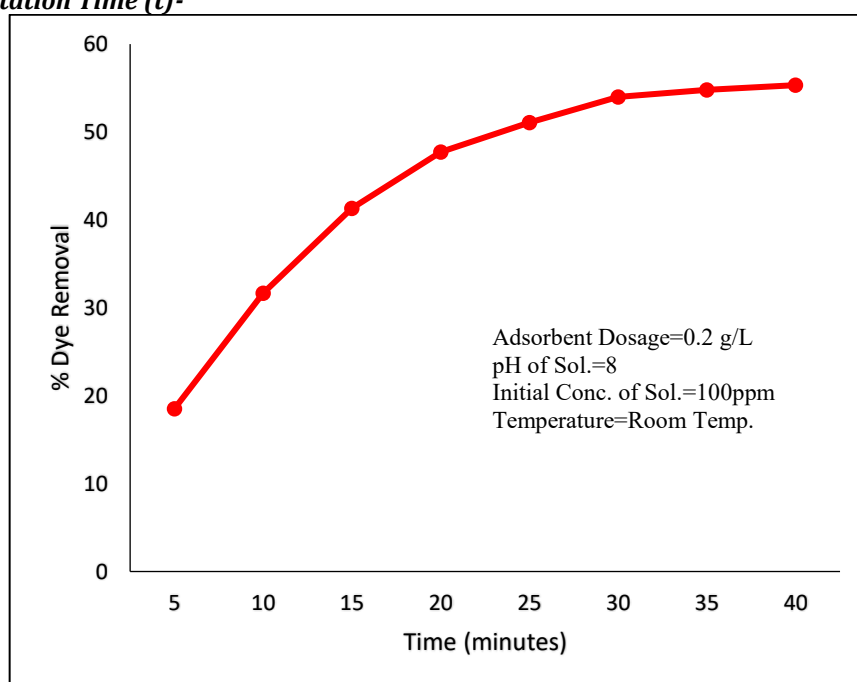


Figure 7- Before and After FTIR images of PA-Zn Nps

3.2 Experimental Parameters:

Experimental data is collected in batch mode using PA-Zn Nps as an adsorbent to investigate the effect of various parameters on Congo Red dye removal from aqueous solution (prepared in the lab). Contact time (t), adsorbent dose (W , g/L), solution pH, initial concentration (C_i , mg/L), and temperature (T , K) are among the factors studied.

3.2.1 Effect of Agitation Time (t)-

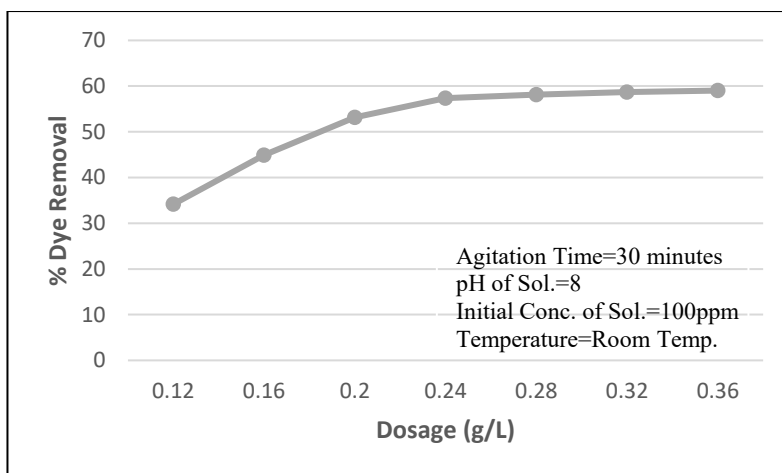


Graph 1- Effect of time on the adsorption of Dye using PA-Zn Nps

The graph depicts time course profiles for Congo Red solution adsorption at 5, 10, 15, 20, 25, 30, 35 and 40 minutes. For future adsorption investigations with varied parameters, the agitation time of this PA-Zn Nps adsorbent has been set at 30 minutes, which is the equilibrium time, as illustrated in graph 1.

3.2.2 Effect of adsorbent dosage (W)-

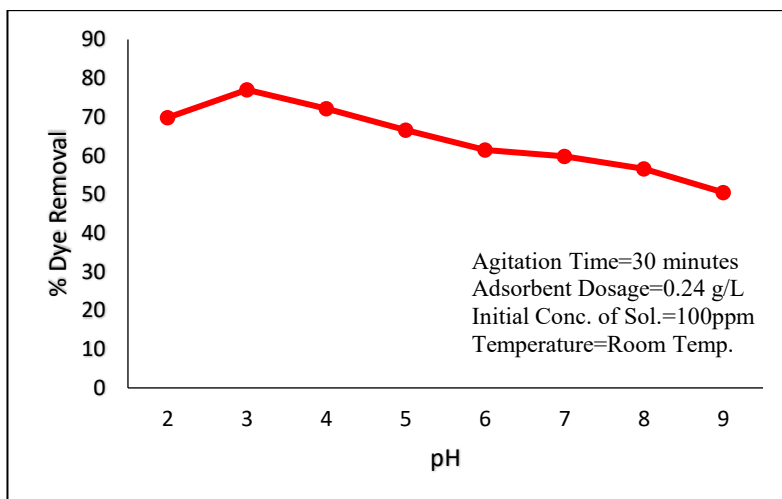
To determine the effect of dose on dye removal, the adsorbent dosage is increased from 0.12 to 0.36 g while all other parameters remain constant. In graph 2, At 0.24 g/L, the greatest percentage removal for a dye solution with 100 ppm is 58.17%. As a result, 0.24 g/L is judged to be the optimal dose for future adsorption tests with varying parameters.



Graph 2- Effect of Adsorbent Dosage on the adsorption of Dye using PA-Zn Nps

3.2.3 Effect of solution pH-

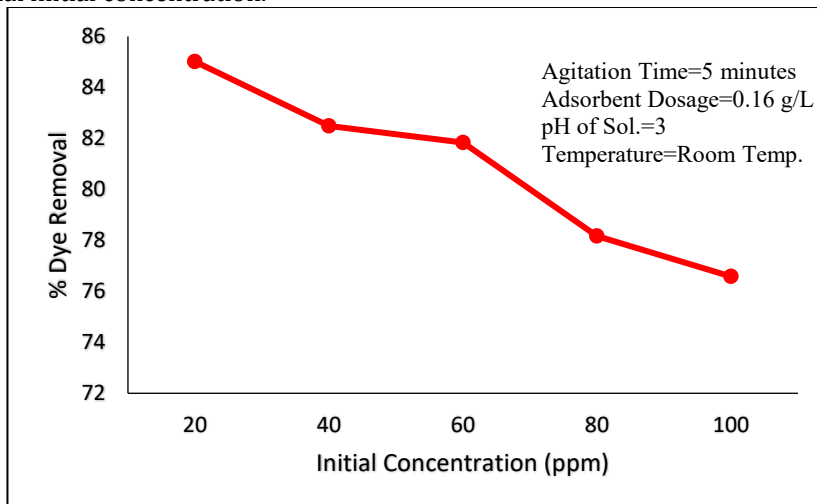
In the adsorption process, one of the most important factors is the solution's initial pH. The effect of the initial pH on the dye's adsorption with PA-Zn Nps from the solution is shown in Graph 3. As a result, the optimal pH was determined to be 3.



Graph 3- Effect of pH on the adsorption of Dye using PA-Zn Nps

3.2.4 Effect of initial concentration of aqueous dye solution-

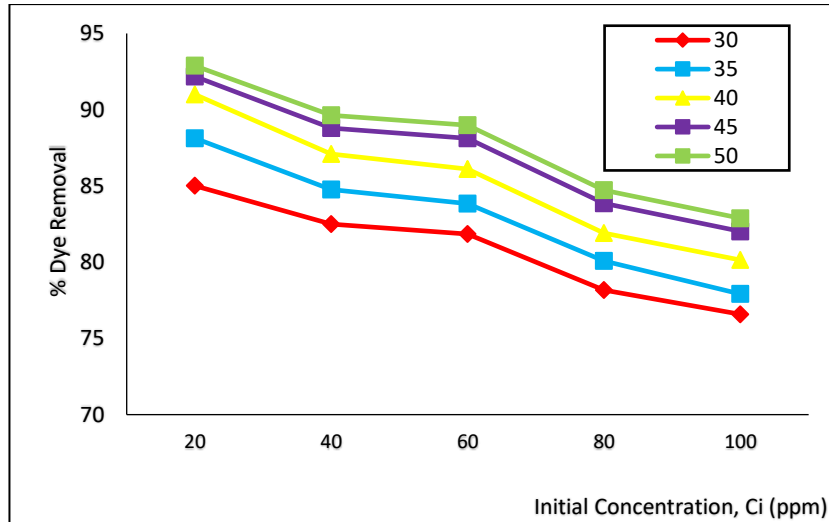
The elimination percentage's variation with initial concentration is seen in Graph 4. The graph demonstrated that the percentage of dye removed reduced as the starting dye concentration rose. Consequently, **20 ppm** is set as the dye solution's optimal initial concentration.



Graph 4-Effect of Initial Concentration on the adsorption of dye using PA-Zn Nps

3.2.5 Effect of Temperature (K)-

The ability of PA-Zn Nps to adsorb dye increased with temperature at various temperatures. Five constant temperatures were used in batch tests to examine the effects of temperature: 30, 35, 40, 45, and 50 degrees Celsius. The percentage of elimination increased with temperature for the initial concentration of 20 ppm, as Graph 5 illustrates. 40°C is determined to be the optimal temperature since this suggests that the adsorption process is endothermic in nature.

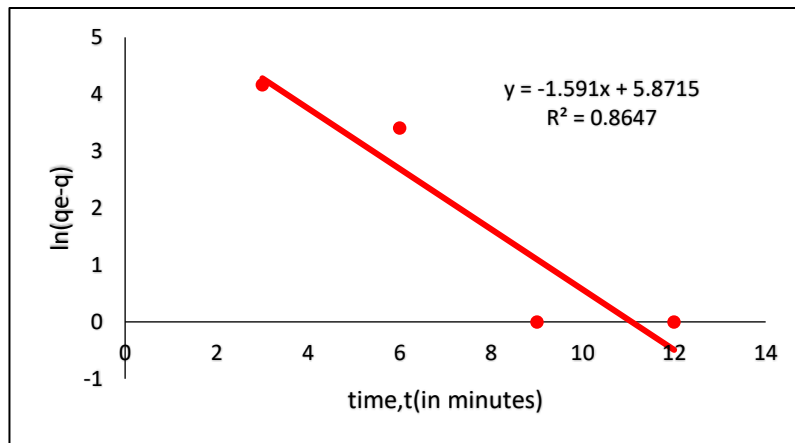


Graph 5- Effect of Temperature on the adsorption of dye using PA-Zn Nps

3.3 Adsorption Kinetics:

3.3.1 Pseudo-first order kinetic model-

$$\ln(q_e - q) = -K_1 t + \ln q_e \quad (1)$$



Graph 6- Pseudo-first order kinetics

A plot is drawn between $\ln(q_e - q)$ and t , which is used to examine the pseudo-first order rate constant k_1 and q_e .

From Graph 6, Slope = $-K_1 = -1.591$

$$K_1 = 1.591 \text{ min}^{-1}$$

$$\text{Intercept} = \ln q_e = 5.8715$$

$$q_e = 354.781 \text{ mg/g}$$

$$R^2 = 0.8647$$

$$\text{The equation obtained: } \ln(q_e - q) = -1.591t + 5.8715 \quad (2)$$

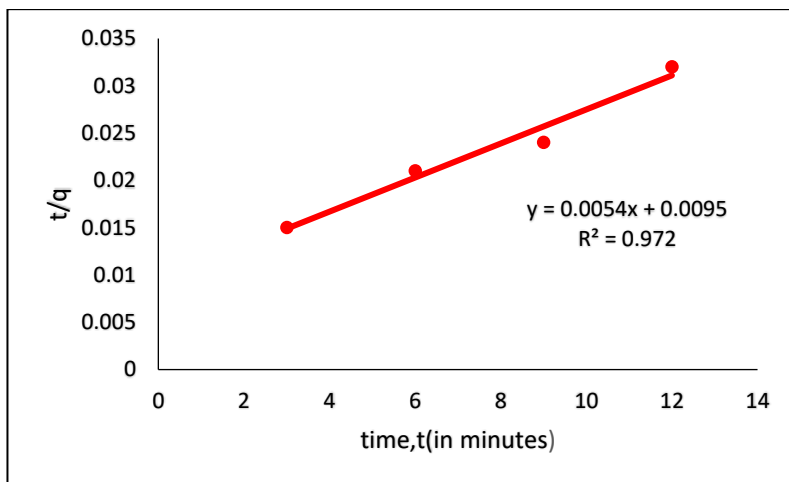
$$\text{From intercept, } q_e(\text{calculated}) \text{ mg/g} = 354.781$$

$$\text{Equilibrium adsorption capacity, } q_e(\text{experimental}) \text{ mg/g} = 84.0099$$

q_e calculated and experimental are not similar. Therefore, we can conclude that pseudo-first order kinetic model is **not an appropriate fit** for this data.

3.3.2 Pseudo-second order kinetic model-

$$\frac{t}{q} = \left(\frac{1}{q_e}\right) t + \left(\frac{1}{K_2} \cdot \frac{1}{q_e^2}\right) \quad (3)$$



Graph 7- Pseudo-second order kinetics

A plot is drawn between t/q and t , which is used to examine the pseudo-second order rate constant k_2 and q_e .

From Graph 7, Slope = $\frac{1}{q_e} = 0.0054$

$q_e = 102.041$ mg/g

Intercept = $\frac{1}{K_2} \cdot \frac{1}{q_e^2} = 0.0071$

$K_2 = 0.0135$ g/(mg.min)

The equation obtained: $\frac{t}{q} = 0.0054 + 0.0095$

From intercept, $q_e(\text{calc}) \text{ mg/g} = 102.041$

Equilibrium adsorption capacity, $q_e(\text{exp}) \text{ mg/g} = 84.0099$

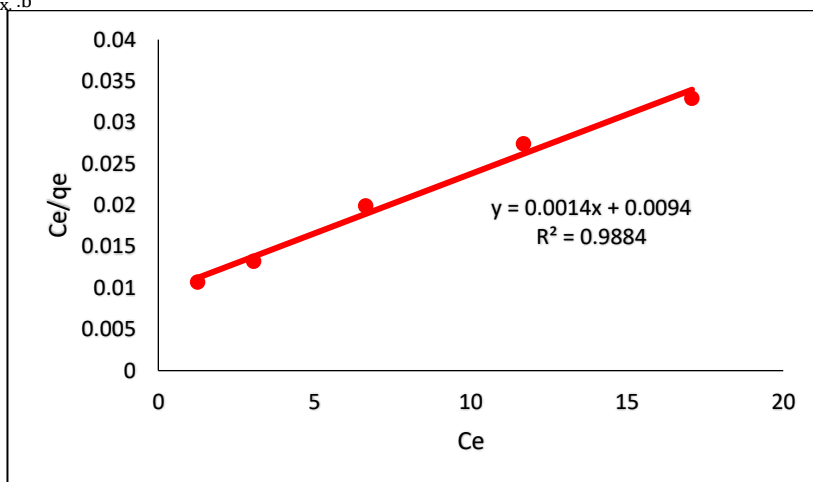
q_e calculated and experimental are similar. Therefore, we can conclude that pseudo-second order kinetic model is a **perfect model** for the adsorption of Congo Red dye using PA-Zn Nps.

3.4 Adsorption Isotherms:

3.4.1 Langmuir Isotherm-

The linear form of Langmuir equation is expressed as:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_{\max}}\right) + \frac{1}{q_{\max} \cdot b} \quad (4)$$



Graph 8- Langmuir Isotherm for adsorption of dye using PA-Zn Nps

A graph is drawn between C_e/q_e and C_e , which is used to examine the Langmuir constant b and $q_{\max}$.

From Graph, Slope = $1/q_{\max} = 0.0014$

$q_{\max} = 1/0.0014 = 714.286$ mg/g

Intercept = $\frac{1}{q_{\max} \cdot b} = 0.0094$

Langmuir Constant, $b = 0.149$ L/mg

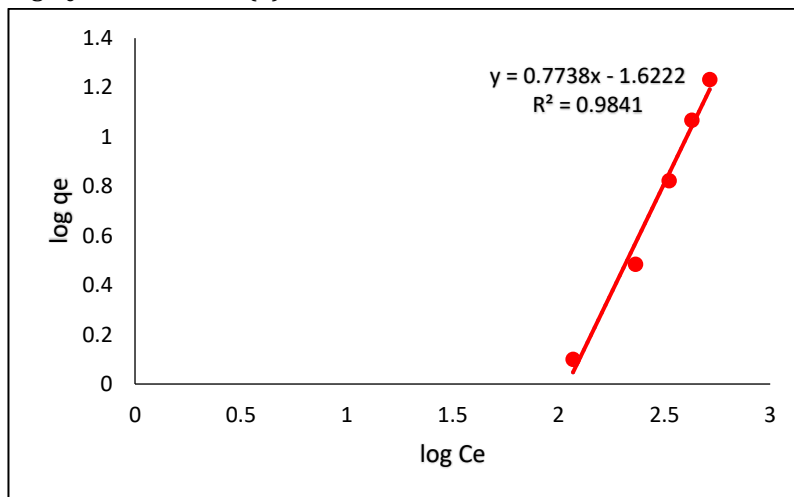
Separation factor or equilibrium parameter, $R_L = \frac{1}{1+bC_0} = 0.0093$

Separation Factor, R_L should be in between 0 and 1, to ensure favourable adsorption. Therefore, we can conclude that Langmuir Isotherm **can be considered** to explain the removal of Rhodamine B dye using PA-Zn Nps since, the obtained value of $R_L < 1$ ($R_L = 0.0093$).

3.4.2. Freundlich Isotherm-

The linear form of Freundlich equation is expressed as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$



Graph 9- Freundlich Isotherm for adsorption of dye using PA-Zn Nps

A graph is drawn between $\log q_e$ and $\log C_e$, which is used to examine the Freundlich constant n .

From Graph, **Slope = $1/n = 0.7738$**

Adsorption Intensity, **$n = 1.2849$**

Intercept = $\log K_f = 1.6222$

Adsorption Coefficient, $K_f = 84.0099 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$

For a Freundlich isotherm to guarantee favorable adsorption, the slope of the adsorption isotherm must be smaller than unity ($1/n < 1$) and the adsorption intensity must be larger than unity ($n > 1$). The " n " number found for the experimental data is therefore more than unity ($n = 1.7721$), indicating that the Freundlich Isotherm Model is the best fit model to describe the adsorption of Congo Red dye using PA-Zn Nps.

4. CONCLUSION

An easy, quick, and environmentally safe method is used to create Ananas Comosus (Pineapple Peel) doped Zinc Nanoparticles (PA-Zn Nps) in order to remove Congo Red Dye, a major staining agent used to stain certain bacteria and examine biofilms or structural components, used as a pH indicator, and historically used to color fabrics. Using PA-Zn Nps as an adsorbent, experimental results for the removal of Congo red dye were acquired. Various experimental runs' results were examined. Temperature, adsorbent dosage, initial dye concentration, agitation time, and initial solution pH all had a major impact on the adsorption efficacy of PA-Zn Nps. The following findings are drawn from the analysis:

- The % adsorption of Dye was maximum at an **Agitation Time of 30 minutes**.
- As the adsorbent dosage rose, the percentage adsorption increased and the **Optimum Dosage is fixed as 0.24 g/L**.
- The plot of pH versus percentage removal of dye showed that the significant adsorption took place at **pH value of 3**.
- The percentage adsorption of dye was decreased with an increase in the initial dye concentration and the **Optimal Initial Concentration of BPA is taken as 20ppm**.
- The percentage adsorption of Congo Red was increased with an increase in the temperature and maximum % adsorption of dye was at an **Optimum temperature of 45°C**.

The adsorption capacity obtained for the optimum conditions is **84.0099 mg/g** for the removal of Congo Red dye using PA-Zn Nps respectively.

The Freundlich and Langmuir isotherm models were proved to be the best adjustment for the experimental data obtained for the adsorption of dye using PA-Zn Nps. The data for the removal of dye using PA-Zn Nps follows the

Freundlich model with the best fit with Adsorption Coefficient, $K_f = 84.0099$ and $R^2 = 0.9841$. The kinetics of the adsorption of dye using PA-Zn Nps can be described better with **pseudo second-order kinetics**. The present work helped in identifying a new source of adsorbent for removal of Congo Dye from effluent water containing low concentrations of the dye.

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