

Copper-Modified Iron Oxide Nanoparticles: A Novel Catalyst for Effective Congo Red Dye Degradation in Wastewater Treatment

ABSTRACT

The raising worldwide water tainting from different sources has delivered admittance to unpolluted drinking water progressively testing. The release of effluents containing colors into water bodies has arisen as a basic ecological worry lately. Regular treatment strategies frequently demonstrate insufficient in wiping out these steady and risky poisons, requiring the investigation of novel methodologies. In this review, Cu-doped FeO nanoparticles were easily blended by means of the co-precipitation strategy, and their synthetic qualities were entirely analyzed. These nanoparticles showed extraordinary adsorption abilities in the corruption of various color compounds. In particular, manufactured acidic color was focused on for expulsion utilizing metal-doped nanoparticles. Ideal boundaries for maximal acidic color not set in stone by surveying the adsorbent portion, beginning color focus, contact time, and temperature. The pH was distinguished as a critical variable, with the best incentive for maximal adsorption of Congo Red Dye viewed as less than 7. As indicated by late discoveries, Cu/FeO nanoparticles displayed unrivaled adsorption limit with regards to Congo Red Dye color at an ideal pH of 2, a measurement of 0.5 g/500 mL, a contact season of an hour and a half, and a color centralization of 150 ppm at 35 degree centigrade. Pseudo second order adsorption kinetic model exhibited amazing fitting outcomes for adsorption energy and balance information.

Keywords: Nanotechnology, Ferric Oxide nanoparticles, Dopping, Adsorption, Coprecipitation method, kinetic, equilibrium modeling.

1. INTRODUCTION

Water is a basic human need, necessary for existence, and closely related to well-being and means of subsistence [1]. In addition to being necessary for human survival, clean water is also a key component of many important industries, such as those that make food, medicine, and electronics [2]. The biosphere faces significant challenges in addition to growing challenges with pure water as freshwater resources become scarcer due to extended droughts, population growth, stricter health-related laws, and conflicting demands from a range of users [3]. Research indicates that only 3 percent of Earth's water is actually freshwater; seawater serves as the most accessible supply of drinking water [4].

By modifying materials at the molecular and atomic levels, nanotechnology aims to create novel structures, processes, or plans with improved electrical, optical, magnetic, conductive, or mechanical qualities [5]. One field where researching nanotechnology as a potentially useful technology has produced amazing achievements is water treatment [6]. Due to their small size, wide surface area, and ease of functionalization, nanostructures present unparalleled opportunities for the development of more effective catalysts and redox active media for wastewater treatment [7].

Dye-based colour repellents offer several advantages over pigment-based ones [8]. Extra dispersion steps are usually not required because colours are highly soluble in solvents. They also feature crisp absorption band, pure colour, and high transmittance due to their

lower particle masses than pigments. Water contamination is largely caused by the textile dyeing industry, which generates a large amount of coloured waste fluids. Colourful wastewater flows are produced by the creation of over 15% of dyes in various textile production processes [9].

Chemicals like dyes (such as azo dyes, triphenylmethane dyes, anthraquinonoid dyes, nitrated dyes, xanthene dyes, phthalocyanine dyes, polymethine dyes, and indigoids) and inorganic compounds are commonly found in textile effluent (metals) [10]. Because of its special characteristics, textile wastewater is one of the most heavily contaminated fluids that needs to be cleansed. Among these qualities are high turbidity, high pH, high quantities of refractory organics, high salinity, and high colour density. If not treated properly, these textile dyes provide serious threats to both human health [11].

The price, ease of usage, and environmental friendliness of the adsorption process have garnered significant attention [12]. "The rise in a substance's concentration at the interface of a condensed and a liquid or gaseous layer due to the action of surface forces" is how adsorption is defined. The adsorbent is the material (surface) that the adsorbate is adsorbed onto adsorbent surface [13]. The adsorbed substance may be in the gas, liquid, or solid state. Based on the types of forces that exist between the adsorbent and the adsorbate, adsorption techniques are classified into physical and chemical groups. Physical adsorption is largely influenced by van der Waals forces, but chemical adsorption is dependent on chemical bonding [14].

During the dye adsorption process, dye molecules are moved from the bulk solution phase to the adsorbent [15]. This is largely because of the designs' flexibility, simplicity, and convenience of use; it's also because of their affordability, insensitivity to dangerous pollutants, and ease of use. Furthermore, no dangerous chemicals are produced during the adsorption process when utilising adsorbents. In general, adsorbents should be able to work in a range of wastewater conditions, be reasonably priced, remove a wide range of contaminants, possess excellent adsorption capabilities, be highly selective for varying concentrations, consume a significant amount of surface area, and be incredibly robust and reusable [16].

Wastewater containing colour is treated using a variety of adsorbents, including polymer-based adsorbents, carbon-based nanoadsorbents, and bio-sorbents [17]. Activated carbon-based adsorbents are the focus of a lot of research in the field of adsorption because of their superior chemical strength, low compactness, structural flexibility, and appropriateness for field-scale applications [18]. Numerous uncommon adsorbents are being investigated as viable, affordable substitutes for pricey adsorbent materials used to remove dangerous pollutants. This includes using readily available natural resources, biodegradable waste, and other waste materials such as industrial, agricultural, and other waste. Many synthetic and natural clays are widely used as adsorbents for colour removal from aqueous solutions because of their low cost, high permeability, high capacity for ion exchange, and lack of toxicity [19].

Congo Red Dye, while commonly used in various industries, poses a significant challenge when it enters wastewater systems due to its persistence and potential environmental hazards [20]. As a responsible member of society, I pledge to raise awareness about the adverse effects of Congo Red Dye on water ecosystems and advocate for sustainable practices to mitigate its impact. By promoting the adoption of efficient wastewater treatment methods and supporting research into innovative degradation techniques, we can work towards safeguarding our water resources from the harmful effects of Congo Red Dye and other pollutants [9].

Metal doped nanoparticles have been produced by the rapid solvothermal approach, chemical spray pyrolysis, chemical vapour deposition, sol-gel, hydrothermal, simple combustion, and co-precipitation methods, among others [21]. Specifically, co-precipitation is a simple, low-cost method for synthesising hetero-atom [22] and simple metal oxides. It involves the mixing of atomic particles, which at low temperatures yields compounds with

perfect stoichiometry. This approach can be used to precipitate pollutants out of solution and build drug delivery systems by encasing pharmaceuticals in nanoparticles [23]. It can also be used to remove toxins from water or the air. Its simplicity and ability to provide good morphological controls make it a popular choice for industrial applications.

One technique that helps to maximise the potential of the raw materials is doping [24]. It ensured that doping ions directly interact with semiconductor oxides to modify their intrinsic properties. Many areas of chemistry, such as the production of catalysts and material modification for energy storage and conversion systems, use doping extensively [25]. The most popular technique for altering the optical and chemical properties of nanomaterials is doping, which is the purposeful introduction of contaminants into the host lattices. At higher concentrations, doping, however, can change the stability and structure of the nanoparticles, changing their properties. Metal-doped nanoparticles are used in a variety of fields, such as electronics, biomedicine, and catalysis [26].

2. EXPERIMENTAL DETAILS

2.1 Material Synthesis

The synthesis of Cu-doped FeO nanoparticles via the coprecipitation method involves carefully controlled addition of aqueous solutions containing iron and copper salts. Typically, iron salt solution, such as iron(II) chloride (FeCl₂) or iron(III) chloride (FeCl₃), and copper salt solution, such as copper(II) chloride (CuCl₂), are mixed in specific molar ratios. These solutions are then combined under controlled conditions, often with the addition of a base such as ammonium hydroxide (NH₄OH) or sodium hydroxide (NaOH) to adjust the pH of the reaction mixture. The reaction is carried out at elevated temperatures, usually around 80-100°C, to facilitate the precipitation of nanoparticles. The precise quantities of chemicals added depend on factors such as desired nanoparticle size, dopant concentration, and synthesis conditions, and are determined through experimental optimization to achieve the desired nanoparticle characteristics [27].

2.2 BATCH ADSORPTION

A stock solution of 1000 ppm was prepared by dissolving 1 g of Congo Red dye in distilled water to a volume of 1000 mL in a measuring flask. From this stock solution, various ppm solutions including 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 50 ppm were created using the dilution formula ($C_1V_1 = C_2V_2$). For the Cu-doped iron oxide nanoparticles, the pH was adjusted using 0.1 M NaOH and 0.1 M HCl. Adsorption tests were conducted to assess the removal efficiency of the Cu-doped iron oxide nanoparticles. Different parameters such as dose rate, concentration, pH, and contact time were examined using adsorbent doses of 0.05 g. Adsorption tests were performed by transferring 50 mL of the working solution with specific pH into 250 mL conical flasks. These flasks were then placed on an orbital shaker for 90 minutes at a speed of 150 rpm. The dose rate effect was investigated using adsorbent doses ranging from 0.05 g to 1 g. The pH effect on Cu-doped iron oxide nanoparticles adsorption was observed at pH 2. The impact of initial dye concentration was assessed at levels of 10 ppm, 20ppm, 30 ppm, 50 ppm, 75 ppm, 100 ppm, and 200 ppm. Contact time was varied at intervals of 5, 10, 15, 20, 30, 45, 60, 90 and 120 minutes at same temperature.

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF COPPER DOPED IRON OXIDE NANOPARTICLES

3.1.1 SEM Analysis

Scanning electron microscopy (SEM) is a powerful tool used to generate detailed images of material samples by scanning a focused beam of electrons over the surface [28]. As the electrons interact with atoms in the sample, various signals are emitted, providing valuable information about the material's composition and surface topography. The electron beam is

scanned in a raster pattern, and the intensity of the detected signal is correlated with the position of the beam to create an image. In the most common SEM mode, secondary electrons emitted by the atoms upon excitation by the electron beam are detected using a secondary electron detector. The proportion of secondary electrons detected, and hence the signal intensity, is influenced by the topography of the sample, among other factors [29].

SEM analysis was utilized to examine the morphology of Cu-doped iron oxide nanoparticles, and the resulting images of the samples are presented below. The Cu-doped FeO nanoparticles appeared as small particles exhibiting significant aggregation and a spherical shape, as observed in the micrographs [30]. Some voids were evident, possibly resulting from the release of hot gases during synthesis. However, further examination at higher magnifications revealed that these aggregated nanoparticles comprised smaller nanoparticles with uniform distribution and spherical clusters [31].

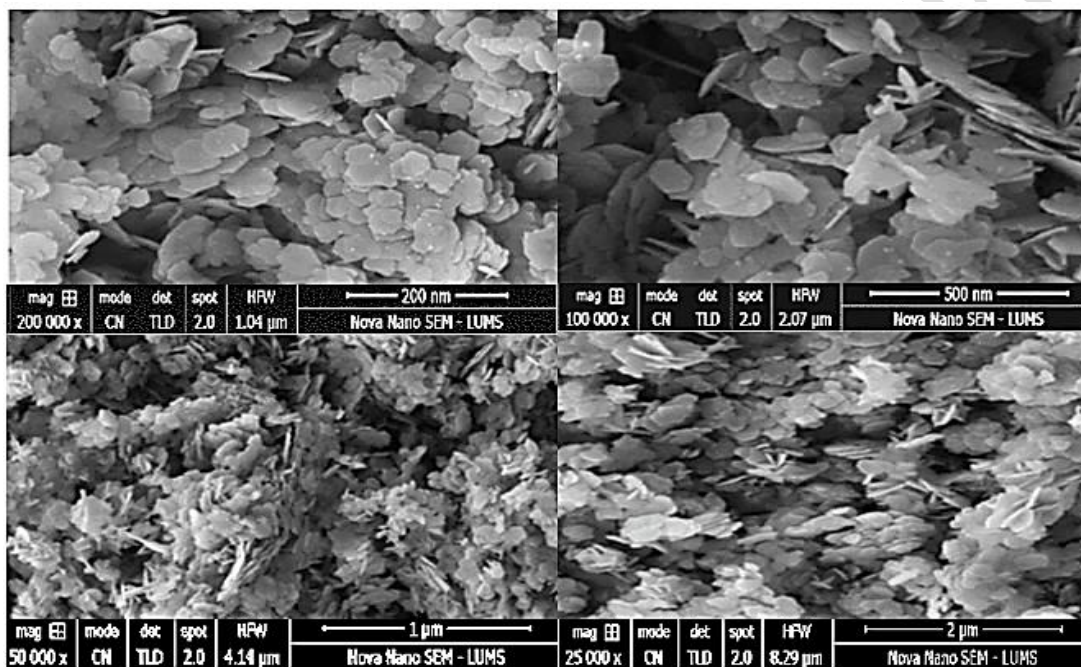


Fig. 1 SEM profile of Cu doped FeO Nanoparticles at different resolution

3.1.2 EDX Analysis

Energy dispersive X-ray spectroscopy (EDX) is a widely employed technique for quantifying and identifying elemental compositions in minute samples, often as small as a few cubic micrometers [32]. When a sample is subjected to an electron beam in a suitably equipped scanning electron microscope (SEM), the atoms on its surface become energized, emitting characteristic X-ray wavelengths specific to their atomic structure [33]. These emitted X-rays are then captured and analyzed by an energy dispersive detector, a solid-state device capable of distinguishing between different X-ray energies. Through this technique, known as EDX, the surface composition of a sample can be determined with high precision [34].

In the conducted research, the EDX technique was utilized to determine the elemental constituents present in the sample based on their atomic and weight percentages. Oxygen, iron, and copper were identified as the predominant components in Copper-doped iron oxide nanoparticles, constituting 70.21%, 25.4%, and 5.01% by weight, and 55.10%, 39.51%, and 5.29% by atomic percentage, respectively. Notably, all elements were detected at their respective characteristic keV values, as revealed by the analysis results [30].

Table 1. Elemental composition

Element	Atomic%	Weight%
O	55.10	70.21
Fe	39.51	25.4
Cu	5.29	5.01

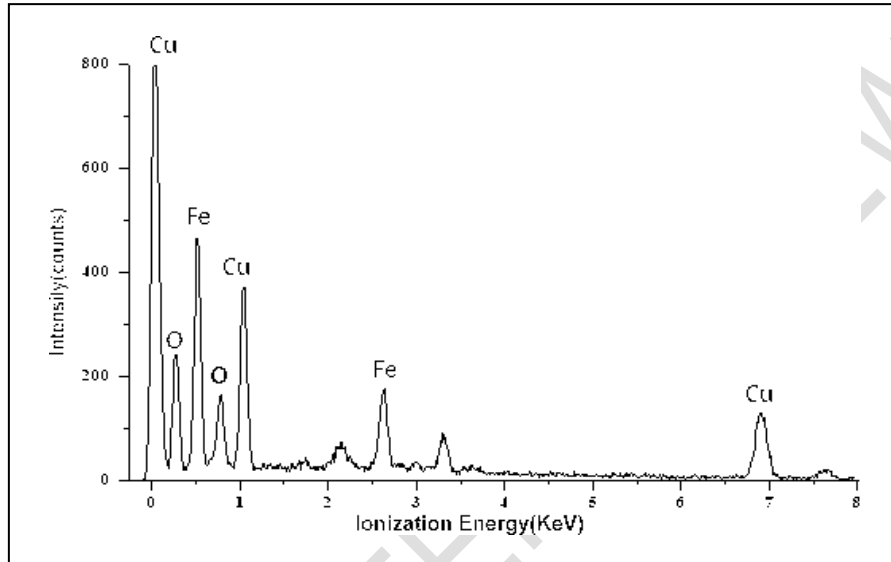


Fig. 2 EDX pattern of Cu doped FeO Nanoparticles

3.2 Calibration Curve

The calibration curves for Congo Red dye were constructed using solutions of varying concentrations prepared with distilled water [35]. The application of Beer-Lambert's law confirmed the linear response of the Congo Red dye calibration curves. According to Beer-Lambert's law principle, the absorbance of a substance is directly proportional to both its concentration and the path length of the light passing through it, resulting in a linear relationship between absorbance and concentration. The Beer-Lambert law equation, expressed as $A = \epsilon cl$, where A is the absorbance, ϵ is the molar absorptivity coefficient, c is the analyte concentration, and l is the path length, further validates the linear nature of the calibration curves for Congo Red dye.

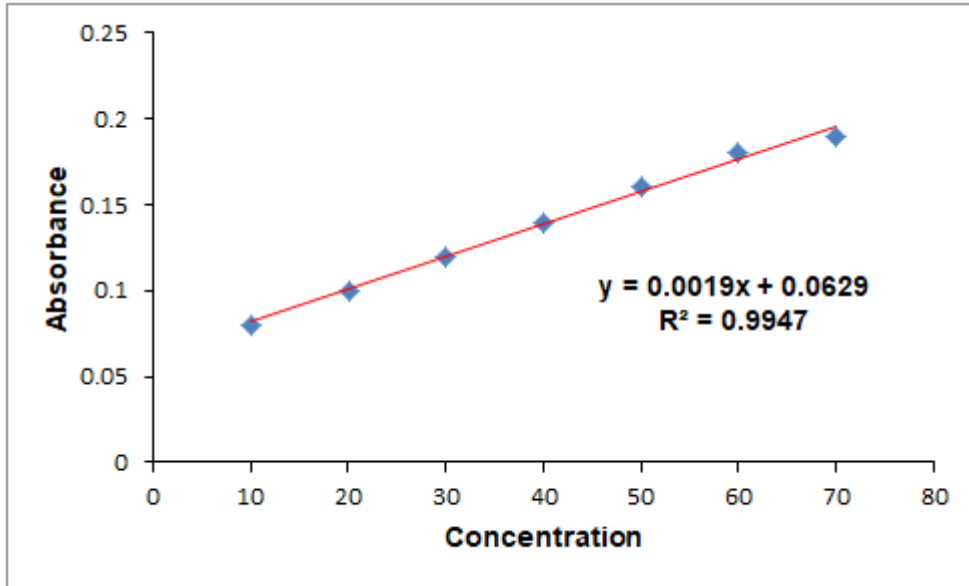


Fig. 3 Optimum Calibration Curve

3.2.1 Determination of Point Zero Charge

The point of zero charge (pHpzc) serves as a pivotal parameter utilized to evaluate the adsorption capacity of the adsorbent surface and discern the type of active binding centers on the surface [36]. It is instrumental in determining whether the adsorbent surface acquires a positive or negative charge with varying pH levels. To elucidate the adsorption mechanism, it is imperative to ascertain the point of zero charge (pHpzc) of the adsorbent surface. Typically, cations are more readily adsorbed at pH levels above the pHpzc, whereas anions exhibit greater adsorbability at pH levels below the pHpzc. Through the solid addition technique, the pHpzc of the Cu-doped iron oxide nanoparticles, which exhibit significant adsorption capacity for Congo Red dye, was determined.

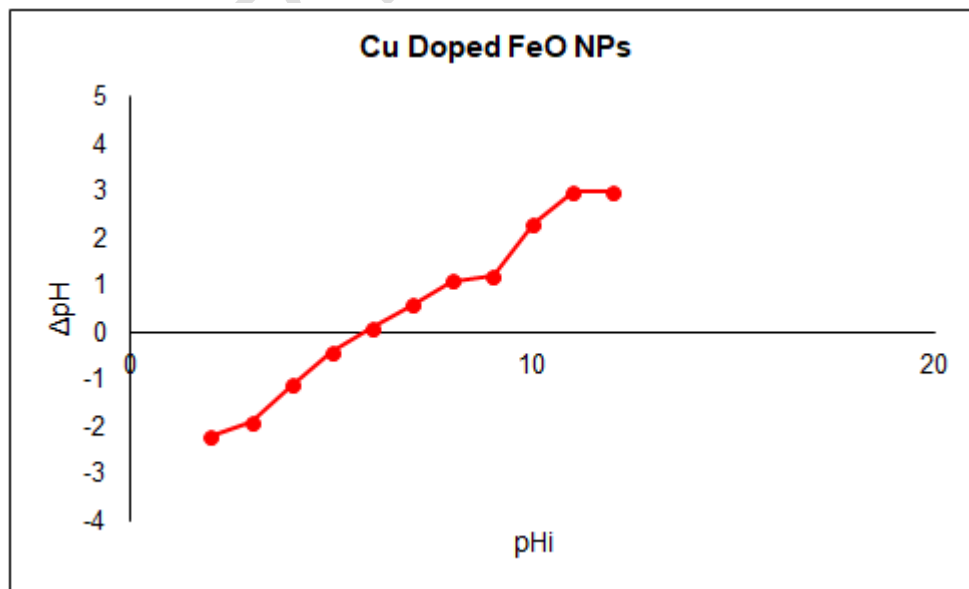


Fig. 4 Point of Zero charge of Cu doped FeO Nanoparticles

Conditions of experiment

Adsorbents = CudopedIronOxidenanoparticles

Optimum pH = 2

concentration = 150ppm

Adsorbent quantity = 0.05g, 0.1g, 0.15g, 0.2g, and 0.25g.

Time = 0 second to 120 minutes

Temperature=35°C

ShakingSpeed=150rpm

3.2.2 Effect of pH

The pH of the solution has a big impact on how the functional groups on the adsorbent's surface change and how soluble dyes are in water [37]. The pH of the effluent is a crucial factor to take into account when assessing the effectiveness of adsorbents for colour removal. Changes in the dye solution's pH cause variations in the ionic forms and surface characteristics of different adsorbents. Anionic dye adsorption is accelerated by lowering the pH of the solution [38]. This is explained by the production of H⁺ ions at the adsorbents' surface sites, which improves the electrostatic interaction between positively charged adsorbents and anionic dyes and raises the adsorption rate. As a result, this improvement raises the dye removal potential. Cu-doped iron oxide nanoparticles were found to have the highest adsorption capacity at pH 2 for the maximum adsorption of Red Congo dye.

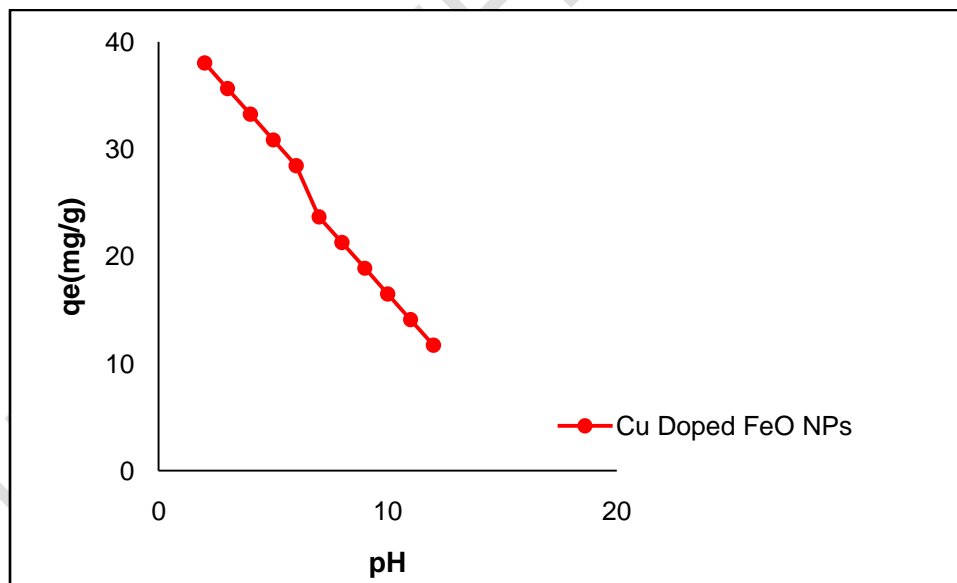


Fig. 5 Effect of pH

3.2.3 Effect of Dose Rate

The study examined the adsorption behaviour of Red Congo dye at different adsorbent dosages (range from 0.05 to 0.5 g) under continuous operating settings with an optimal pH of 2, temperature of 35°C, dye concentration of 150 ppm, and agitation speed of 110 rpm [39]. Although all other parameters stayed constant, there were variations in the adsorption capacity of Cu-doped iron oxide nanoparticles when the dosage of the adsorbent was

changed from 0.05 to 0.5 g. The most significant amount of dye removal was achieved when 0.05 g of Cu-doped iron oxide nanoparticles were used, according to the results [40].

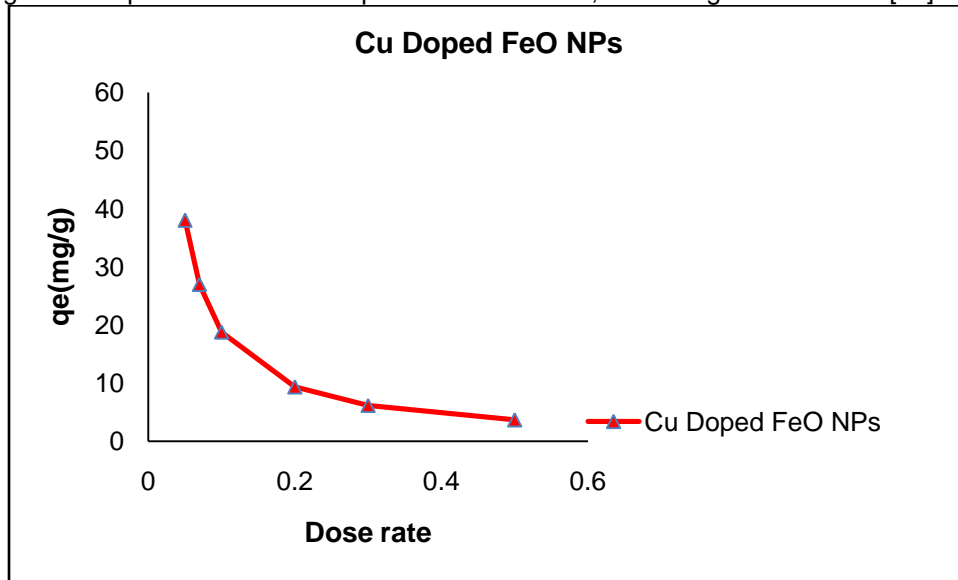


Fig. 6 Effect of Dose Rate

3.2.4 Effect of Contact Time

The efficacy of dye absorption and removal is largely dependent on the length of time that Red Congo dye and Cu-doped iron oxide nanoparticles interact. Adsorption is a time-dependent process that can provide information about how to create and use efficient adsorption systems. Cu-doped iron oxide nanoparticles were used in batch adsorption experiments with contact times varying from five to ninety minutes in order to clarify the effect of contact time on adsorption processes. Cu-doped iron oxide nanoparticles adsorbed Red Congo dye quickly at first, then more slowly, and finally, after 120 minutes, they reached equilibrium. The adsorption rate decreased as contact duration increased, which was explained by a decrease in the number of active binding sites that were available at saturation and a subsequent drop in adsorption capacity.

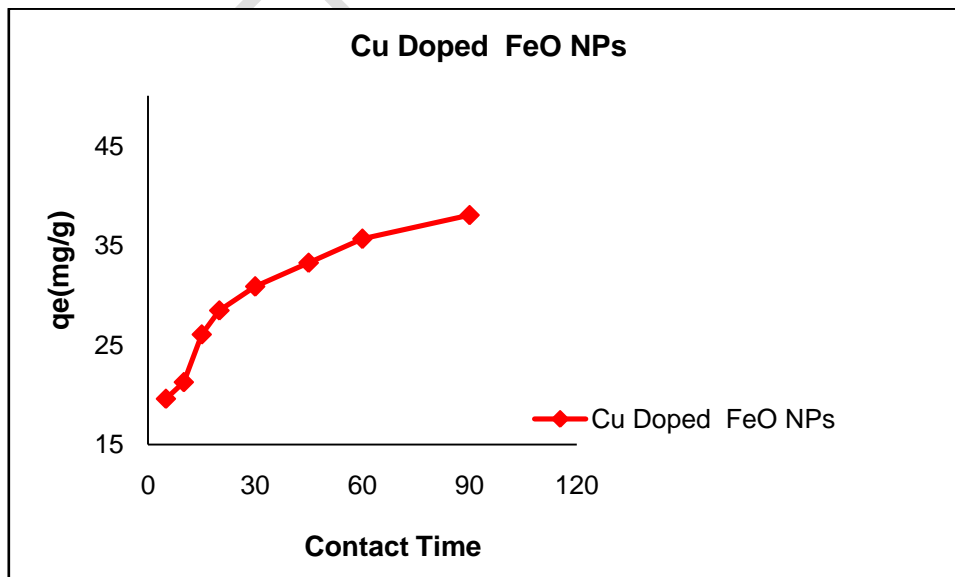


Fig. 7 Effect of Contact Time

3.2.5 Effect of Initial Concentration

The capacity of the cu doped iron oxide nanoparticles to adsorb is significantly influenced by the dye solution's starting concentration. For cu doped iron oxide nanoparticles with a 0.05g dose amount, various concentrations of 10 ppm, 25 ppm, 50 ppm, 75 ppm, 100 ppm, and 150 ppm solutions were produced at an ideal pH of 2. The maximum adsorption capacity of cu doped iron oxide nanoparticles was observed at 150 ppm, despite the dye concentration increasing.

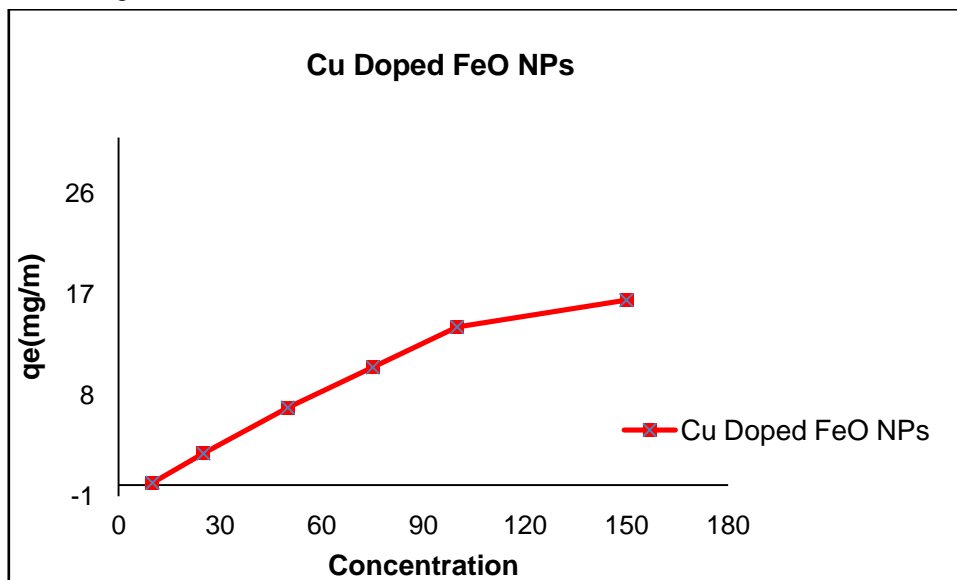


Fig. 8 Effect of Concentration

4. KINETIC MODELS

A fundamental trademark that offers important experiences into response pathways and potential purposes is the assimilation of adsorbates. To explore this ingestion interaction, different dynamic models, like first-request and second-request, have been utilized to examine information on the assimilation conduct of Corrosive Congo Red Dye across various adsorbents.

4.1 Pseudo 1st Order Kinetic Model

The first-order can empower rearrangements of the assimilation peculiarities. As per first-order conditions, the adjustment of color focus over the long run is precisely relative to P1. The following is pseudo-first order direct incorporated condition.

$$\log (q_e - q_t) = \log q_e - K_1 t \quad \text{Eq. (1)}$$

Here, the pseudo-first request rate consistent, meant by the letters k1, subs for the pseudo-first request rate steady. T represents time (min). Hypothetical qualities for qe and k1 were gained by plotting the chart between log (qe - qt) and t, and these qualities were then determined from incline and block.

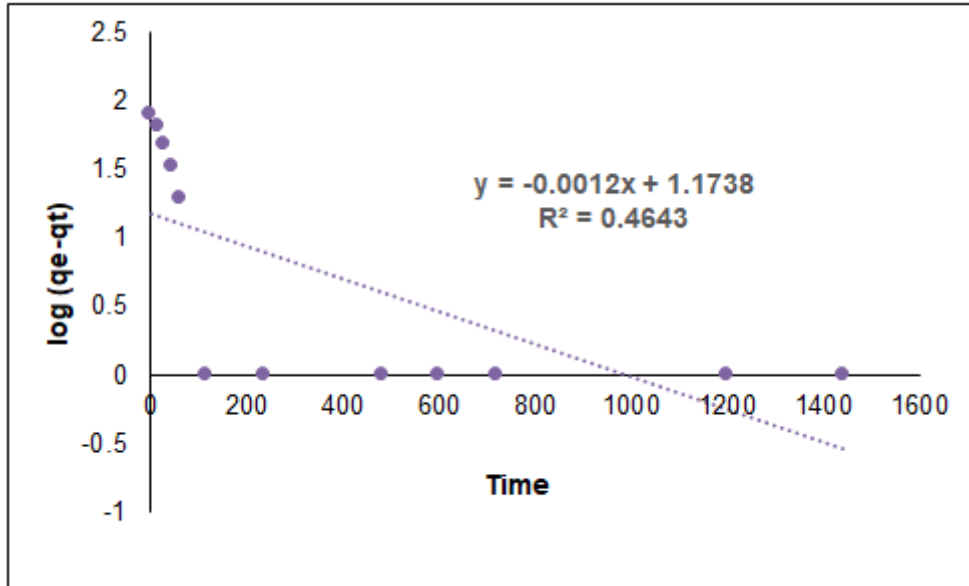


Fig. 9 Pseudo 1st order kinetic model for adsorption of Congo Red Dye

4.2 Pseudo 2nd Order Kinetic Model

Effective utilization of second request empowers comprehension of the assimilation cycle during the entire contact term. Given is second order differential condition

$$dq/dt = K_2 (q_e - q)^2 \quad \text{Eq. (2)}$$

Here, k_2 represents sorption interaction's second request rate steady. Following communication and utilizing limit conditions second order straight structure is given as

$$\left(\frac{t}{qt}\right) = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq. (3)}$$

The hypothetical adsorption limit second-request rate steady, k_2 , as well as the catch and incline, might be determined by plotting t/qt versus t . The upsides of k_2 , $q_{e,cal}$, $q_{e,exp}$, and R^2 for the adsorption of Congo Red Dye utilizing Cu doped iron oxide nanoparticles are recorded underneath.

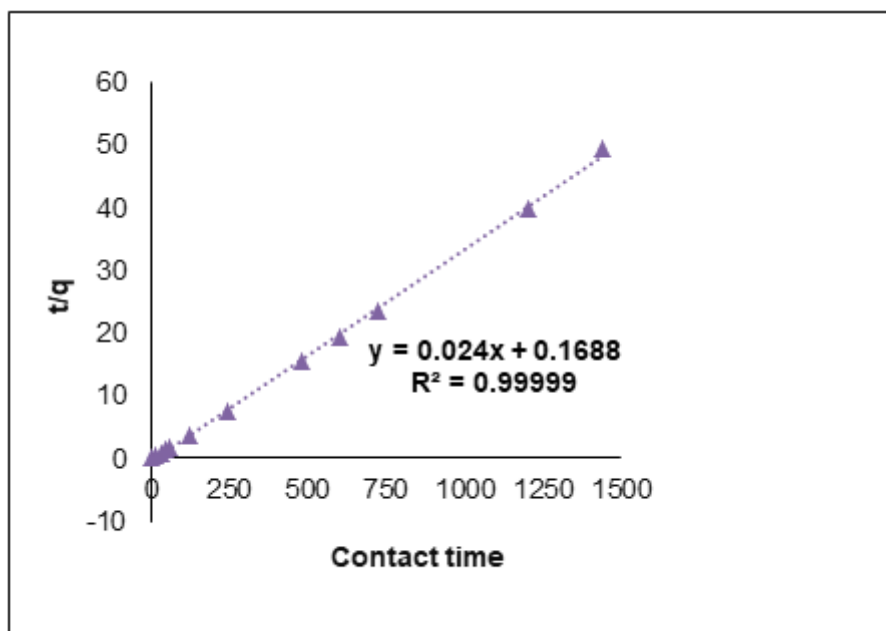


Fig. 10 Pseudo 2st order kinetic model for adsorption of Congo Red Dye

Table 2: Data for pseudo first and second order for adsorption of Congo Red Dye onto Cu/FeO Nanoparticles

		Pseudo first order model		Pseudo second order model		
q _e (exp) (mg/g)	q _e (cal) (mg/g)	K ₁ (min ⁻¹)	R ²	q _e (cal) (mg/g)	K ₂ (g mg ⁻¹ min ⁻¹)	R ²
41.56	78.98	0.00052	0.4643	41.6667	0.003412	0.999

As seen by the outcomes' connection coefficient (R²=1), a pseudo-second request motor model may be utilized to make sense of the dynamic information. Be that as it may, the pseudo-second request motor model performed fundamentally better when utilized with the dynamic information. The connection coefficient (R²) for the pseudo-first request dynamic model is the most minimal of the adsorbent used to degrade Congo Red Dye. However the pseudo-second order dynamic model beat the pseudo first order model.

4. CONCLUSION

Water makes up around 76% of the planet's surface, making it essential for animal life and growth. The polar ice caps, which hold 2% of the freshwater on Earth, retain 90% of the planet's water. One of the most fundamental problems in the creation of flow is perhaps the tainting of our water source. The different manmade materials that darkened wastewater carried made it extremely dangerous for people, animals, and aquatic life. Cu/FeO nanoparticles were synthesized using coprecipitation method to degrade Congo Red Dye in dirty water.. The pseudo-second order model best contributed to the overall understanding of the Congo Red Dye Degradation. For treating wastewater with acidic hues, the aforementioned nanoparticles have been considered the most energy-efficient, naturally occurring, practically applicable, and organically replenishable materials.

6. Declarations

Ethical Approval: Not applicable (NA)

Availability of data and materials: Not applicable (NA)

Ethics approval/declarations: Not applicable (NA)

Consent to participate. NA

Consent for publication. NA

Availability of data and material/ Data availability. NA

Code availability (software application or custom code). NA

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