

Original Research Article
**Efficient Adsorption Kinetic Studies of
Chromium from effluents using *Ziziphus
Mauritiana* Leaf extract mediated TiO₂
Nanoparticles**

ABSTRACT

Water plays a remarkable role in the natural structure of a living organism as people's bodies comprise 60% water by weight. Water contamination due to negative industrialization and anthropogenic activities is a huge hazard to humanity. The water quality is degraded by the discharge of organic and Inorganic compounds, Pathogens, herbicides, pesticides, drugs, heavy metals, and macroscopic pollutants in the water bodies, leading to a decrease in the oxygen in the water. Heavy metals are well-defined habitat pollutants because of their toxicity and bio accumulative nature. The adsorption method is more appealing to researchers because of its extraordinary potential to remove toxic metals. In the current research, the plant leaf extract of *Ziziphus mauritiana* was subjected to synthesize TiO₂. For Chromium removal from an aqueous solution, TiO₂ nanoparticles will be used. UV-Visible, FTIR, powder and SEM will be employed to characterize nanoparticle synthesis. Atomic Absorption Spectrophotometer will be employed for heavy metal removal analysis before and after adsorption. pH, dosage rate, concentration, and contact time were among the various experimental activities used. Finally, to improve the results, experimental statistics were applied to all recorded data.

Keywords: Nanotechnology, Green synthesis, Titanium dioxide nanoparticles, Ziziphus Mauritiana leaves, Adsorption, Kinetic and Equilibrium Modeling

1. INTRODUCTION

Water is essential for survival as it is only second to oxygen as a key ingredient of life on earth. It is widely regarded as both a universal solvent and a life elixir. The water cycle is also necessary for the biodiversity and food chain of our planet to survive[1]. Aquatic pollution is the discharge of potentially harmful effluents in aquatic mediums like oceans, lakes, rivers, canals, etc. Organic and inorganic wastes, pathogens, dyes, drugs, chemicals, heavy metals, herbicides, and fungicides are the effluents that degrade the water quality. These effluents deplete the oxygen content of water, causing anaerobic degradation and aquatic life death. When pollutants consumption levels exceed a certain limit, a variety of disorders and abnormalities are triggered. Water quality problems, such as oxygen depletion, pH changes, and an increased microbial population, have an immediate effect on aquatic life[2].

Some heavy metals are released into the air during combustion or as effluents into the soil or water bodies, while others are used in industry for diverse industrial purposes. These metals through amplification get involved in the food chain and thereby exert influence on human beings as well. The stipulation of pollution-free water has perturbed the wastewater treatment methodologies and emerging technologies. Dyes, drugs, heavy metals, organic and inorganic moieties can be eliminated through contaminated water

bodies by adopting methodologies of flocculation, filtration, degasification, filtration, precipitation, photocatalysis, and adsorption[3].

Living organisms require essential heavy metals like copper, nickel, iron, and zinc to carry out basic processes like body growth, cell metabolism, and organ development, which are only needed in trace amounts(10-15ppm). Heavy metals which are non-essential such as lead(Pb), mercury(Hg), cadmium(Cd), and others are discharged into the atmosphere by natural and anthropogenic sources like industrial effluents, automobile exhaust, and mining, which are not needed even in trace amounts. Because heavy metals are extremely soluble in aquatic environments, they can be easily absorbed by living organisms. These poisonous metals are non-biodegradable and have an affinity for accumulating in living organisms[3].

Chromium is a trace mineral that is necessary for human survival. Chromium is divided into two types: trivalent, which is non-toxic to humans, and hexavalent, which is hazardous[4]. The illustration depicts the metal's poisonous toxicity as well as its polished mirror shine. Industrial catalysts and pigments are made of chromium compounds. Humans require chromium because it aids in the utilization of glucose. It is, however, poisonous in excess.

Hexavalent compounds are the primary cause of both acute and chronic chromium toxicity. Chromium hexavalent compounds have significant toxic effects of contact and inhalation such as dermatitis, allergic and skin reactions, skin and ulcerations, discoloration of teeth, perforation of the nasal septum, and asthmatic reactions. Chromium compounds (CaCrO_4 , Na_2CrO_4) have harmful effects on the lungs' protective mechanism[5]. Hexavalent compounds pass through the cell membrane and are reduced to trivalent metabolites that can bind to proteins[6]. These metabolites become trapped and accumulate within the cell. Experiments were also carried out in order to better understand the kinetics of chromium removal using various approaches.

The four main methods for treating wastewater are physical water treatment, biological water treatment, chemical treatment, and sludge treatment. To separate poisonous pollutants from aquatic pollution, a variety of traditional techniques such as precipitation, coagulation, filtration, reverse osmosis, ion exchange, solvent extraction, sedimentation, adsorption, and electrochemical methods have been used, but these techniques are ineffective due to their high operational costs and low accuracy. Chemical precipitation and coagulation-flocculation can be used to treat wastewater with metal concentrations greater than 1000 mg/L[7].

Researchers prefer the adsorption procedure to traditional approaches because it is more cost-effective and straightforward[8]. This technology offers a lot of potential for removing hazardous metals from industrial and household wastes while also improving the ecosystem's quality. The emergent technologies in the adsorption method have upgraded the removal efficiency by implementing nano-adsorbents, magnetic adsorbents, and metal oxide adsorbents. When liquid molecules bind to the surface of a solid substance, this is known as adsorption. Adsorbates are molecules or ions, whereas adsorbents are solids used for adsorption. Adsorbents have a large interior surface area, which allows them to adsorb.

In this work, we used a straightforward, environmentally friendly synthesis method to create TiO_2 nanoparticles by employing *Ziziphus mauritiana* leaf extract as a reducing agent. Then, synthetic TiO_2 nanoparticle characterization is carried out. In the end, kinetic and equilibrium modelling improved the results.

2. EXPERIMENTAL DETAILS

2.1 Materials Synthesis

In the first step of the green synthesis process, *Ziziphus mauritiana* leaf extract was prepared. Phenolic compounds present in this leaf extract act as capping agents or reductants which **reduced** the titanium metal. Isopropanol has been used to aid nanoparticle synthesis. About 30g of fresh Leaves of *Ziziphus mauritiana* were collected from the

Botanical Garden of the University. Leaves of *Ziziphus mauritiana* were washed through tap water to clean them with dust particles. The washed leaves of *Ziziphus mauritiana* were dried in the shade to ensure that all of the moisture in the leaves was gone. To make powder, the dried leaves were crushed and the ground in a pestle mortar. 25grams of ground leaf powder was weighed by using weighing balance. The weighed ground powder was mixed in with 150ml of refined water in a 250ml estimating **utencil**. The **recepticle** was then placed on the hot plate for half hour at 80°. After boiling, the entire mixture was allowed to cool at ambient temperature. After that, the filter paper was placed on the funnel, and the resulting extract was filtered. And then leaf extract was stored in a refrigerator for further use.

In second step 25ml of Titanium Isopropoxide salt was dissolved slowly in 25ml of isopropanol in a 250ml tapered flagon. This combination was mixed with an attractive stirrer for 30 minutes. Then 25ml leaf extract was dropped slowly within 1 hour with the help of a burette with continuous stirring. To prepare the 2M solution of NaOH 0.8g of NaOH was dissolved in 100ml distilled water. Almost 3 to 4 drops of prepared 2M solution of NaOH were added to the mixture to provide a basic medium. And the 25ml cold distilled water was added to the mixture slowly within 1 hour with continuous stirring. The whole mixture was stirred for 4 hours until the fine particles were formed in the form of precipitates. The solution was kept overnight until two layers were formed. The upper layer was removed with the help of a sucker and the rest particles were centrifuged so that all the liquid content was removed. After that, the particles were kept in a petri dish to oven dry. After drying at 120° for four hours, particles were calcined in a muffle furnace at 400° for 4 hours. Finally, a white powder of TiO₂ nanoparticles was obtained.

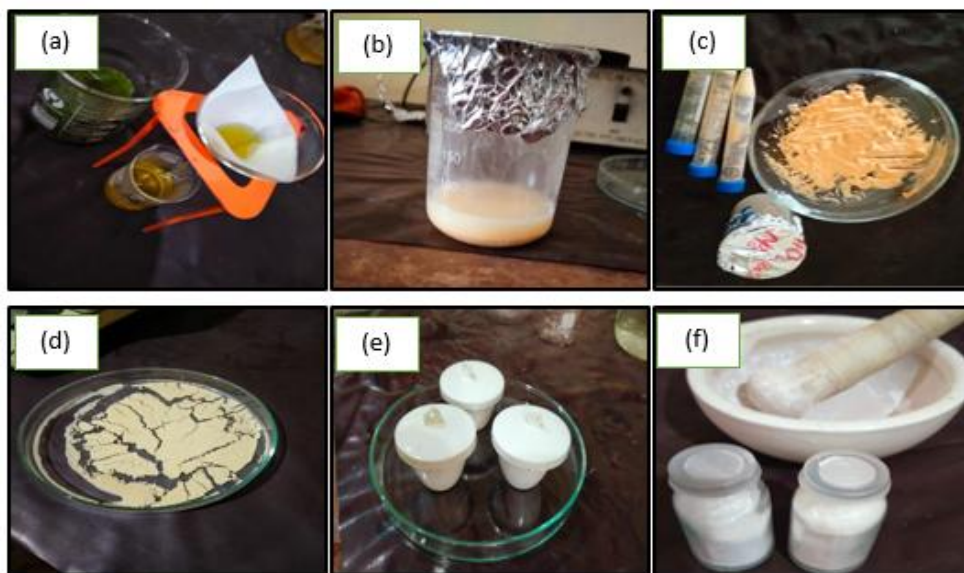


Fig. 1. Green Synthesis of TiO₂ nanoparticles (a) *Ziziphus mauritiana* leaf extract, (b) layers formation, (c) centrifugation, (d) dried powder, (e) calcination, (f) TiO₂ nanoparticles

2.2 BATCH SORPTION EXPERIMENT

To set up a 1000ppm stock arrangement of chromium, 2.8289g of potassium dichromate was broken up in 1000ml refined water. 2g of chromium salt was disintegrated and was put in a 1000ml round bottom flask. Adsorption tests were carried out to determine the removal efficiency of adsorbents such as TiO₂ nanoparticles for chromium. Working solutions of 50ppm in 2000ml distilled water were prepared from stock solutions using the dilution

formula($C_1V_1=C_2V_2$). For the pH adjustment of working solutions, 0.1M HCl and 0.1M NaOH were prepared. Different parameters of dose rate, concentration, pH, and contact time were applied to investigate the adsorption of chromium. Adsorption tests were performed by taking 100ml of working solution with specific pH in 250ml conical flasks. All the conical flasks with samples were placed in an orbital shaker for 2 hours at the speed of 130rpm. The dose rate effect was investigated with all adsorbents doses of 0.05g, 0.1g, and 0.15g. 0.2g, 0.25g. For chromium adsorption, the pH effect was observed at pH 1,2,3 and 4. Initial concentrations were also varied at 10ppm, 25ppm, 50ppm, 100ppm, 200ppm, 400ppm. Contact time was varied at the interval of 0sec and 15, 30, 45, 60, 120, 240, 480, 600, 720, 1200, 1440 minutes.

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF TiO₂ NANOPARTICLES

3.1.1 UV-Visible spectroscopy

TiO₂ Nanoparticles were achieved through the green synthesis procedure by using the leaf extract of *Ziziphus mauritiana* leaf and isopropanol. White-colored precipitates were found. Nanoparticles blend was affirmed when white-colored precipitates were shaped. TiO₂ nanoparticles were also certified by including a UV-Visible Spectrophotometer which shows optical properties in the extent of 200-400nm recurrence. TiO₂ nanoparticles show the most noteworthy absorbance at 280nm which is referred to in the composition and certified by the plan of TiO₂ nanoparticles[9]. The green incorporated TiO₂ nanoparticles show serious solid areas for a band at 280nm and a delicate ingestion band at 236nm credited to the electron progress from the valence band to the conduction band. The band opening energy by extrapolating the curve is seen as around 3.6 eV[10].

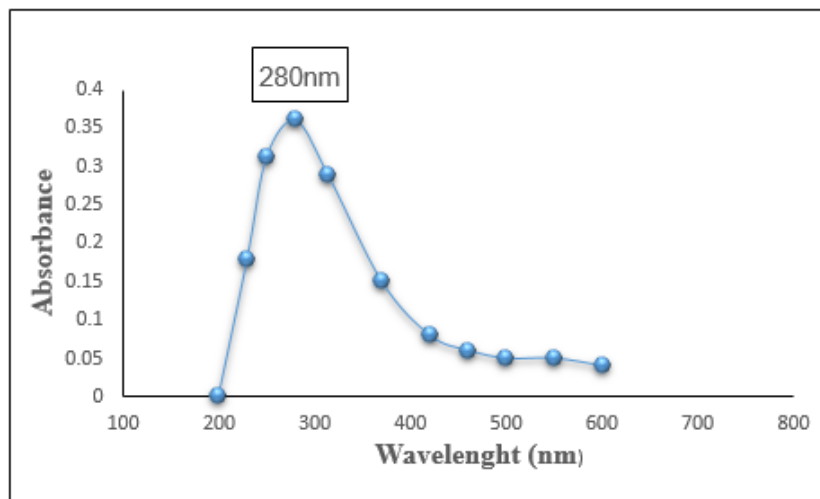


Fig.2 UV-Visible spectrum of TiO₂ NPs

3.1.2 Fourier Transform Infrared spectroscopy

The FTIR confirms that a compound contains a variety of practical groupings. When a molecule absorbs IR radiation, it produces a variety of vibrational states. A vibrational shift occurs, resulting in a little change in the frequency of the compound's useful groupings. The tops of the FTIR range of TiO₂ nanoparticles are 1641cm⁻¹, 690cm⁻¹, and 518cm⁻¹. At 3000-3500cm⁻¹, the extending band of TiO₂ nanoparticles' hydroxyl collection should be observed. Water Ti-OH twisting modes are represented by the next band at 1630cm⁻¹. A solid band at 1641cm⁻¹, which demonstrates Ti-O-Ti functional group, and a sharp top at 650cm⁻¹, which compares to Ti-O modes, were also seen.

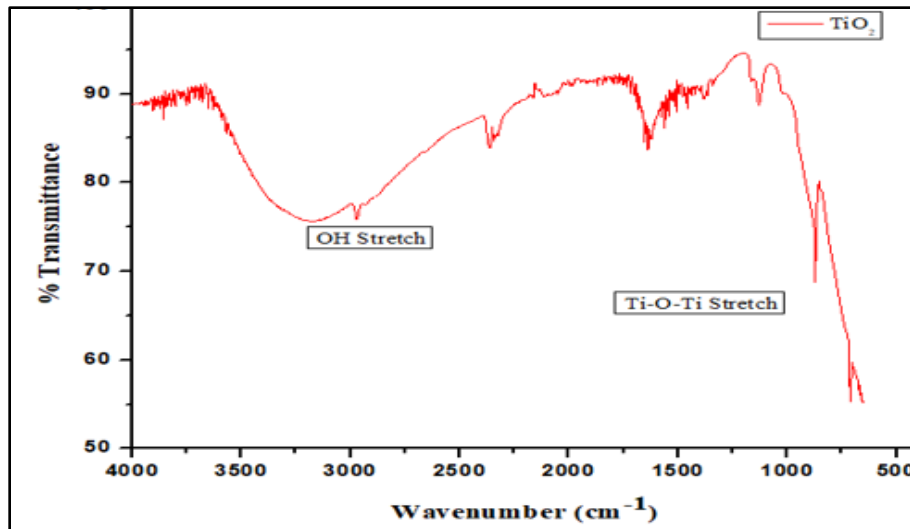


Fig.3 FTIR spectrum of TiO₂ NPs

3.1.3 Scanning Electron Microscopy

SEM is versatile best-in-class equipment that is commonly used to examine material surface irregularities. SEM, for example, is a high-energy electron beam that provides data on geology, morphology, structure, and science, making it a useful tool for material organization. Geography refers to an item's surface characteristics such as smoothness, perfection, and harshness, whereas morphology refers to an item's shape and size. Also, while crystallography refers to the designs of an object in material, composition refers to the components and combinations that make up the substance.

In the SEM profile of TiO₂ nanoparticles, round particles with agglomeration were identified, as shown in the inset of the figure. This study discovered that TiO₂ nanoparticles in suspension form agglomerates due to the irregular morphology of primary particles, implying that a competent scattering expert should be able to obtain a highly scattered suspension of TiO₂ nanoparticles.

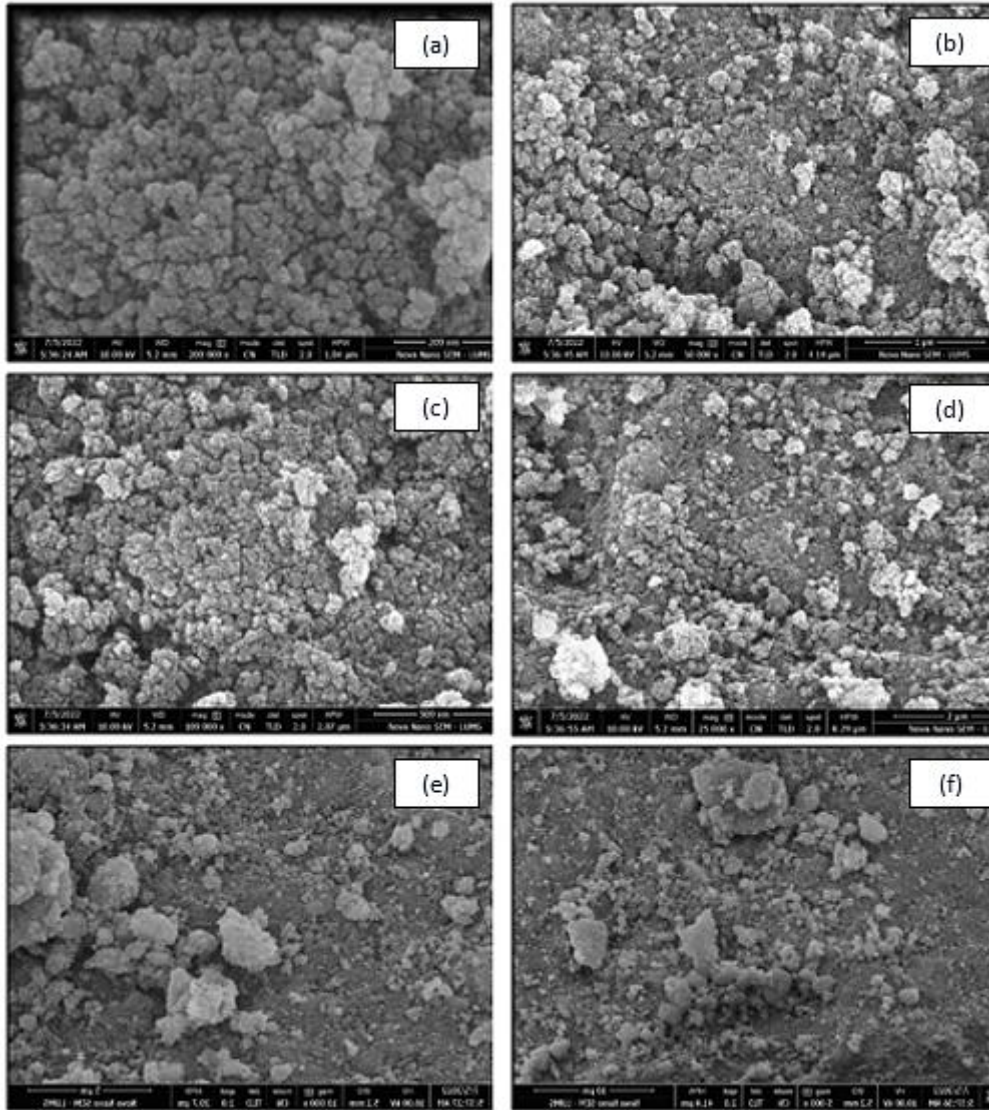


Fig. 4 SEM analysis of TiO₂ nanoparticles with magnification range of 200nm(a), 500nm(b), 1µ(c), 2µ(d), 5µ(e), 10µ(f)

3.2 CALIBRATION CURVE

The calibration curves of chromium were plotted using solutions of various concentrations generated with distilled water. Beer Lambert's law confirms the linear response of the chromium calibration curves. The Beer-Lambert law principle states that a material's absorbance is proportional to its path length and concentration and that the calibration curve is shaped like a straight line[11]. Where A is the absorbance, is the molar absorptivity coefficient, c is the analyte concentration, and L is the route length, the equation of Beer Lambert's law is shown below.

$$A = \epsilon cl \tag{1}$$

Table 1. Optimum calibration values for Chromium metal

Sr. No.	Concentration (ppm)	Absorbance of Cr
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1	2	0.693
2	6	0.2049
3	8	0.2592
4	12	0.3745

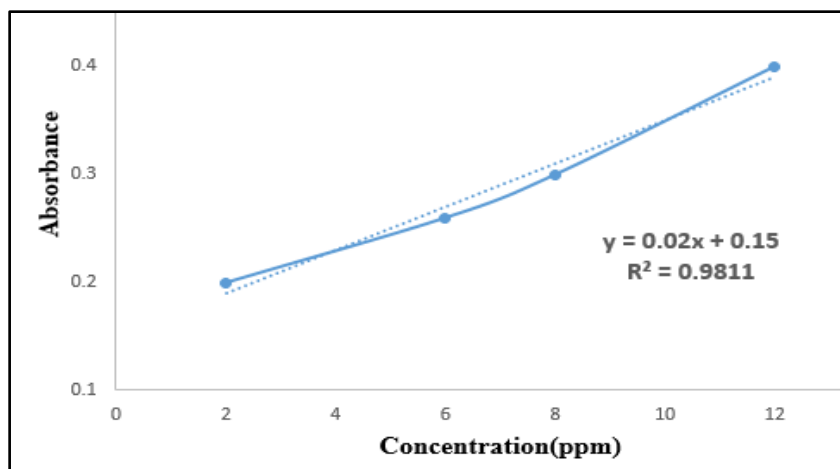


Fig. 5 Calibration curve for chromium

3.3 EFFECT OF pH

Protonation and deprotonation[12] of the groups present at the surface of the adsorbent govern the surface charge density when the pH changes. It has been reported that pH is the most important factor influencing heavy metal adsorption characteristics[13], as it controls the solubility of heavy metal hydroxides, phosphates and carbonates, as well as the hydrolysis of heavy metals in organic matter and sediments, dissolved clay surface charge variations, and the creation of ion pairs.

Using TiO₂ nanoparticles, the impact of pH on the adsorption of chromium was investigated in this study. The maximum chromium removal efficiency was recorded at pH= 2. For chromium, TiO₂ nanoparticles had a 68 percent removal rate at pH=2 and dropped at decreasing pH.

Conditions of the Experiment

Adsorbent = TiO₂ nanoparticles, Amount of Adsorbent = 0.05g, pH = 1-4, Concentration = 50ppm, Shaking time = 2 hours

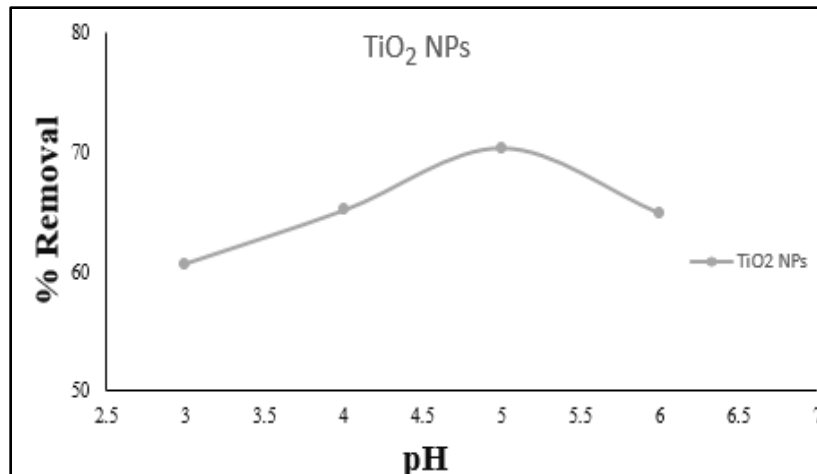


Fig. 6 Effect pH on chromium

3.4 EFFECT OF DOSE RATE

Another important factor in adsorption is the dose rate[14]. The working solution for chromium was kept at a pH of 2 with a starting concentration of 50 ppm. The experiment was carried out at dose rates of 0.05g, 0.1g, 0.15g, 0.2g, and 0.25g, with removal efficiency measured. The maximal uptake of chromium was measured at 0.25g dose at its respective optimal pH. It was discovered that as the adsorbent dose increased, so did the removal efficiency. This means that as the adsorbent dose increases, so do the available adsorption sites for Chromium ion, resulting in higher removal efficiency. For chromium, TiO₂ nanoparticles showed 80.91 percent removal rate.

Conditions of experiment

Adsorbent = TiO₂ nanoparticles, Dose quantity = 0.05g – 0.25g, Concentration = 50ppm, pH for chromium = 2, Shaking time = 2 hours

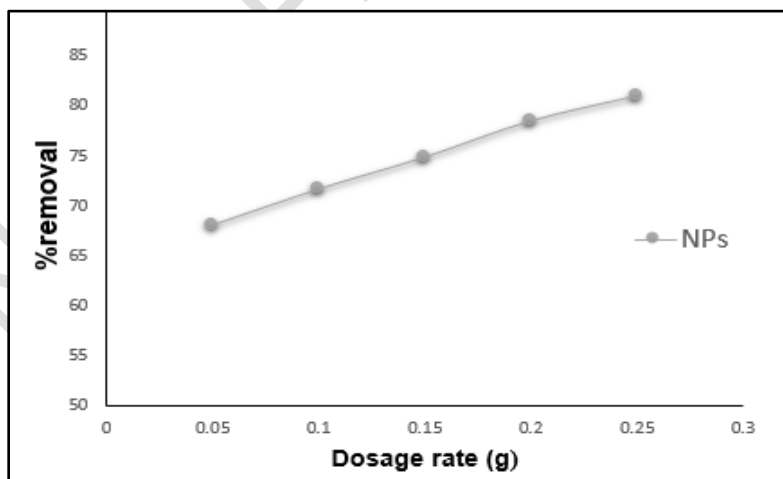


Fig. 7 Effect of dose rate on Chromium

3.5 EFFECT OF CONCENTRATION

In this work, the impact of a change in starting concentration on the removal of chromium was investigated. Different concentrations of 10ppm, 25ppm, 50ppm, 100ppm, 200ppm, and 400ppm solutions were generated at optimum pH of 2 for chromium with a 0.05g dose

quantity. The highest chromium removal was recorded at 100ppm, with decreasing removal as concentration increased.

The removal effectiveness reduces as the concentration rises or falls above or below 100ppm, as seen in the tables. Because this mechanism is dependent on active sites, there are fewer active sites for adsorbate molecules at greater concentrations

Conditions of Experiment

Adsorbent = TiO₂ nanoparticles, pH for Chromium = 2, concentration = 10,25,50,100,200,400ppm, Shaking time = 2 hrs, Amount of adsorbent = 0.05g

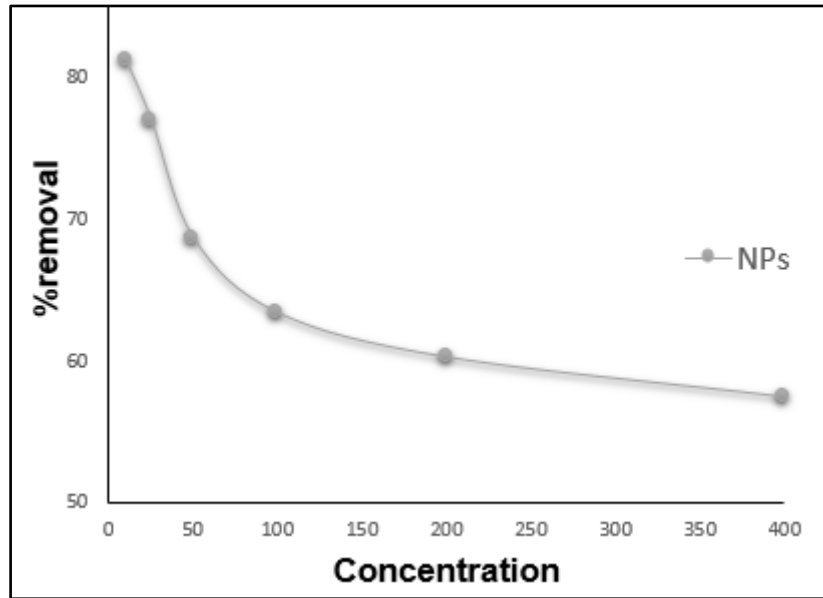


Fig. 8 Effect of Concentration on Chromium

3.6 EFFECT OF CONTACT TIME

The most significant factor influencing the adsorption parameter is contact time[15]. Adsorption rate increases as the contact between adsorbent and adsorbate increases[16]. The surface of the TiO₂ nanoparticles were all subjected to kinetic analysis. 0sec, 1,15, 30, 45, 60, 120, 240, 480, 600, 720, 1200, 1440 min were used to record the effect. The removal efficiency increases as the time interval grow until equilibrium is reached. Gradual increases were recorded up to 10 hours after equilibrium was reached and a straight line could be seen on the graph. At the optimum contact time, most materials were removed.

Conditions of experiment

Adsorbent = TiO₂ nanoparticles pH for chromium = 2, pH for Chromium = 2, concentration = 50ppm, Adsorbent quantity = 0.05g, time = 0 second to 1440 minutes

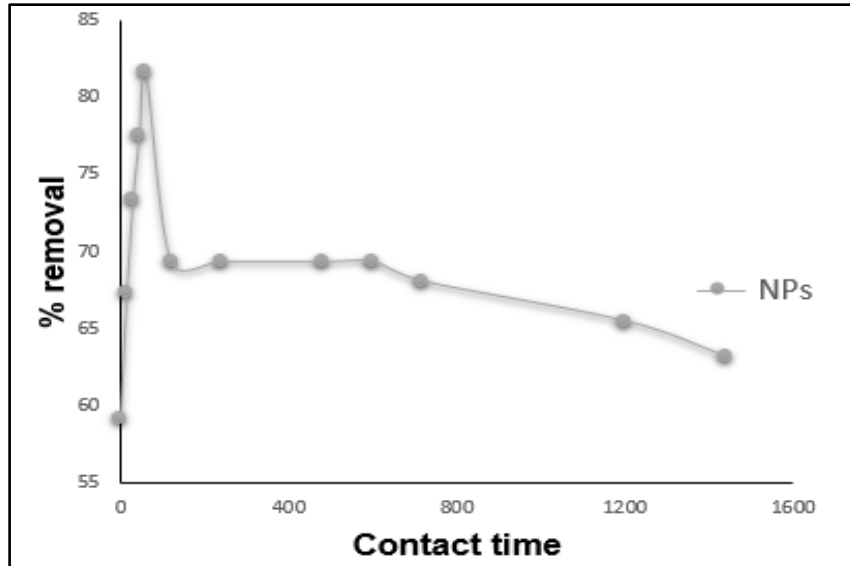


Fig. 9 Effect of Contact time on Chromium

3.7 EQUILIBRIUM MODELING

The use of equilibrium sorption equations to analyse experimental results can occasionally reveal information about the mechanism or mode of adsorption as well as adsorbent properties. At different concentrations, different isotherm models express the equilibrium between the adsorbed heavy metals on the adsorbent and the unadsorbed component remaining in solution. The adsorption process' chemistry is extremely complex.

3.7.1 Langmuir isotherm

In the Langmuir model, maximum monolayer adsorption limit q_m (mg/lg) and different not altogether firmly established from the linearized sort of condition, and the data for chromium didn't follow the Langmuir isotherm successfully[17].

$$\frac{C_e}{q_e} = \frac{1}{KL \times q_m} + \frac{C_e}{q_m} \quad (2)$$

Where C_e is equilibrium heavy metal concentration in the aqueous phase, q_m is for complete monolayer adsorption capacity mg/g. K_L is Langmuir's constant. Adsorption is expected to occur at a particular homogeneous surface with an adsorbate[18]. When the adsorbate particle covers a site, no further adsorption process takes place.

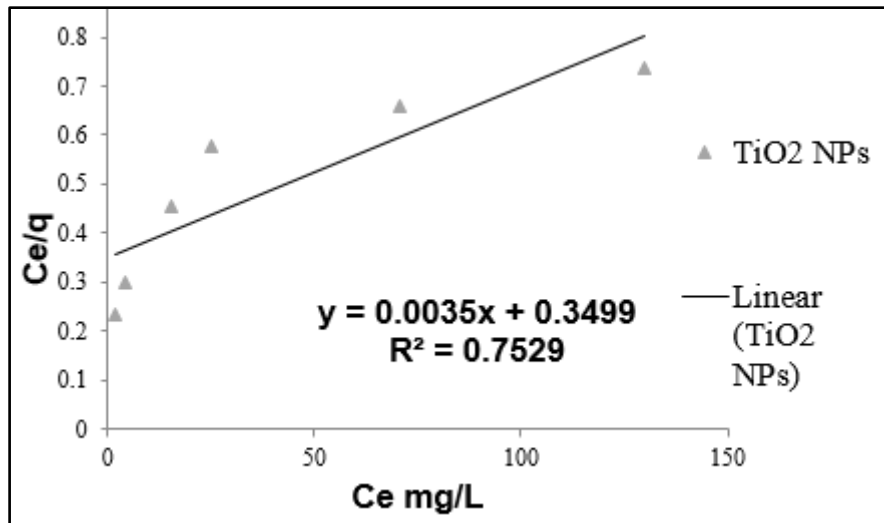


Fig. 10 Langmuir Adsorption Isotherm of Chromium

3.7.2 Freundlich isotherm

According to the empirical equation

$$\ln(qe) = \frac{1}{n} \ln Ce + \ln(Kf) \quad (3)$$

The Freundlich isotherm is based on the sorption of a ligand on a heterogeneous surface of a sorbent[19].

A value of $1/n$ below one or n larger than one implies facile separation and advantageous multilayer adsorption of heavy metal ions from an aqueous media. K_f value denotes the adsorption capacity of the adsorbent. A better adsorption and the development of a substantially stronger connection between the heavy metal and adsorbent are indicated by the smaller value of $1/n$ that was achieved. In non-ideal sorption on a heterogeneous surface and multilayer sorption[20], Freundlich isotherm is used, which implies that the binding sites are not equal and/or independent.

The maximum R^2 is close to 0.99, and $q(\text{exp})$ is much closer to $q(e)$, indicating that the data followed the Freundlich isotherm and that adsorption occurs with multilayer formation rather than monolayer formation[21]. Because it revealed a more linear behavior than the Langmuir model owing to its better R^2 values for chromium metal, the results suggested that the Freundlich model is appropriate for equilibrium modelling. This was determined by comparing the two models. The value of the correlation coefficient in the Freundlich model is quite close to one.

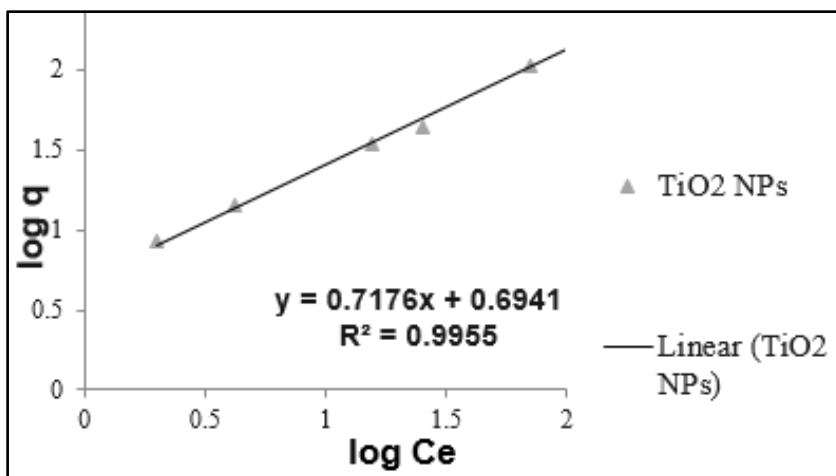


Fig. 11 Freundlich Adsorption isotherm of Chromium

Table 2 Comparison between Langmuir and Freundlich Adsorption isotherm of Chromium

Adsorbent (NPs) Adsorbate (Cr)	Langmuir model			Exp. Value	Freundlich model			
	X_m (mg/g)	K_L (L/mg)	R^2		q (mg/g)	Q_e (mg/g)	$1/n$	K_F (mg/g)
	285.71	1	0.75	176	162.57	0.71	-0.36	0.99

3.8 KINETIC MODELING

The rate that governs the time of contact, one of the main properties that reveals the adsorbent's removal capacity, is influenced by chromium kinetics. The transportation of chromium molecules onto each adsorbent has been explained using kinetic equations[22]. Kinetic models, Pseudo 1st order and Pseudo 2nd order were applied to observed data to investigate the mechanism of chromium adsorption.

3.8.1 Pseudo 1st Order Kinetic Model

Typically, it is written as the equation

$$\ln(q_e - q_t) = \log q_e - Kt/2.303 \quad (4)$$

Where q_t mg/g is the quantity of sorption at time t and q_e is the amount of sorption at the point of equilibrium and K_1 (min^{-1}) is the pseudo first order adsorption rate constant. The graphs of $\log(q_e - q_t)$ VS t were used to get the K_1 and q_e values. The rate is assumed to be proportional to the number of vacant sites in the model. The first order rate constant K_1 and equilibrium adsorption capacity q_e were determined using the slopes and intercepts of the plot of $\log q_e - q$ VS t . The image makes it abundantly evident that the experimental adsorption capacity q , Experimental value cannot be predicted by the pseudo first order equation.

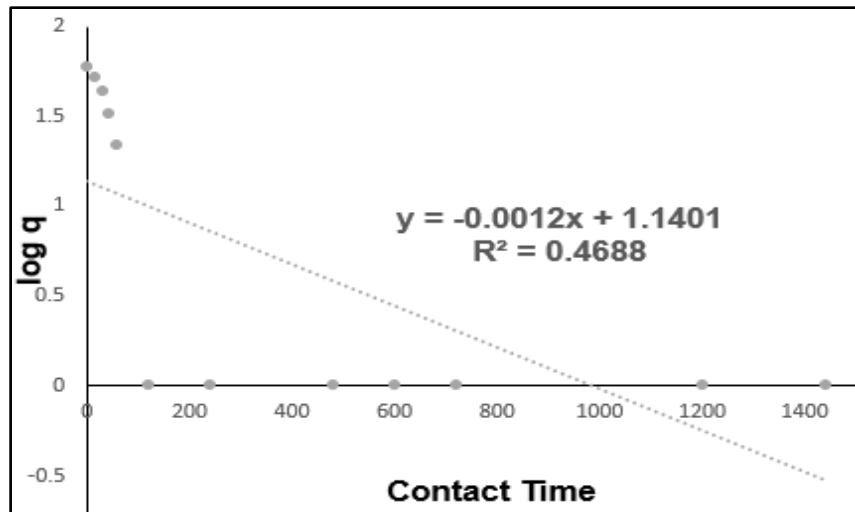


Fig.12 Pseudo 1st order kinetic model for adsorption of Chromium

3.8.2 Pseudo 2nd Order Kinetic Model

The pseudo-second order equation is typically written as

$$t/q_t = 1/K_2q_2^2 + 1/q_2t \quad (5)$$

If pseudo-second order, K_2 (mg/g) is the adsorption rate constant, and K_2 and q_e can be calculated from the intercept and slope of the t vs. q_t plot. The pseudo-2nd order kinetics model was used to further evaluate the adsorption kinetics data[23]. The adsorption is thought to be precisely proportional to the square of the number of vacant sites, according to the model[24].

According to the study's findings, pseudo first order and second order rate equation kinetic formulations are candidates for providing an adequate explanation for the investigated adsorption systems. For the kinetic data of Chromium for adsorbent, the correlation coefficient R^2 obtained from the pseudo first order rate equation and the second order rate equation demonstrates that the second order rate equation is the best suited model. The vast majority of previous researchers developed a pseudo second order kinetic model to characterize the process of cation sorption on various adsorbents.

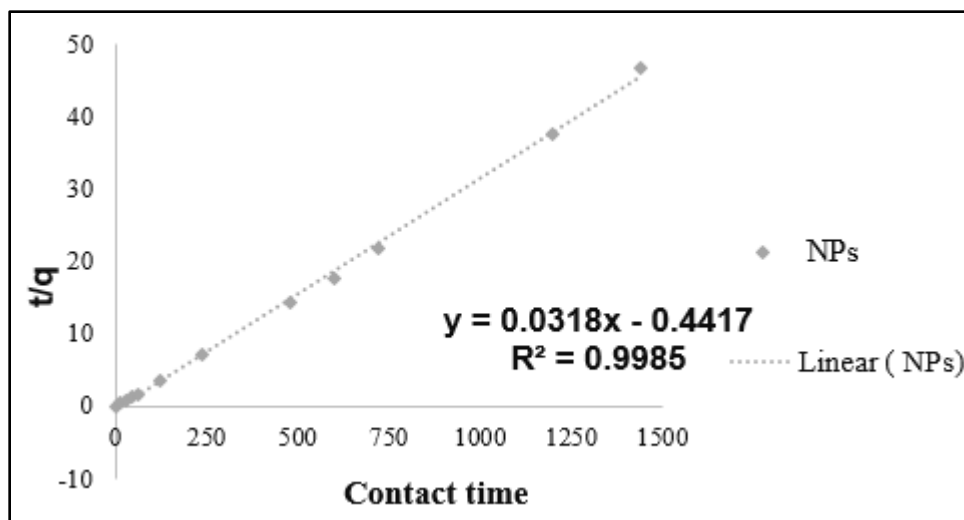


Fig 13 Pseudo 2nd order Kinetic Model for adsorption of Chromium

4. CONCLUSION

Water is essential for survival as it is only second to oxygen as a key ingredient of life on earth. Organic and inorganic wastes, pathogens, dyes, drugs, chemicals, heavy metals, herbicides, and fungicides are the effluents that degrade the water quality. To separate poisonous pollutants from aquatic pollution, a variety of traditional techniques such as precipitation, coagulation, filtration, reverse osmosis, ion exchange, solvent extraction, sedimentation, adsorption, and electrochemical methods have been used, but these techniques are ineffective due to their high operational costs and low accuracy. Researchers prefer the adsorption procedure to traditional approaches because it is more cost-effective and straightforward. The goal of the research was to synthesis of TiO_2 nanoparticles to adsorb chromium. For the characterization certain techniques such as UV-Visible, FTIR. and SEM were employed. pH, dosage rate, concentration, and contact time were among the various experimental activities used. Maximum chromium and lead elimination was seen at a pH of 2 for chromium. For chromium metal that have exhibited maximal elimination at various concentrations, an optimal value of 100ppm was discovered. For maximal metal removal, an optimum dose quantity of 0.25g was discovered. Similarly, 10 hours optimum contact time was discovered, with maximum elimination percentages in various time intervals. Finally, to improve the results, experimental statistics were applied to all recorded data.

5. 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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