

INDUSTRIAL WASTEWATER TREATMENT METHODS

1. INTRODUCTION

In recent years, the availability of clean water has become a pressing issue globally, affecting both developed and developing nations. Over 1.1 billion people lack access to improved water sources, while 2.6 billion people face inadequate sanitation [1]. Water consumption has significantly increased, from 1,382 km³ per year in 1950 to an estimated 5,235 km³ per year by 2025. By then, water availability is projected to fall to about 872 m³ per capita annually, well below the 1,000 m³ per capita thresholds that defines water-scarce regions [2]. This growing water scarcity is a critical environmental challenge, expected to impact 3.5 billion people i.e.48% of the global population by 2025[3]. As populations grow, the diminishing availability of fresh water will hinder socio-economic development in many countries. To combat this, reusing wastewater is emerging as a vital strategy to augment water resources, provided it can be managed safely [4].

Industrial wastewater treatment typically involves multiple stages aimed at removing contaminants. The municipal wastewater treatment process consists of three main steps: primary (physico-chemical processes like precipitation and sedimentation), secondary (biological treatment such as activated sludge or trickling filters), and tertiary (sand filtration and polishing)[5]. Sewage wastewater contains a variety of contaminants, including suspended solids, organic matter, microorganisms, nutrients, heavy metals, and increasingly, pharmaceutical residues [6]. The activated sludge process, commonly used in wastewater treatment plants (WWTPs), leads to increased sludge production around 9 million tons in Europe by 2005 posing environmental and economic challenges. Disposing of and treating sludge can account for up to 50% of WWTP costs [7]. Moreover, conventional treatment processes struggle with efficiency, time, and cost, and excess nutrients like phosphate and ammonium nitrogen in the effluent can cause eutrophication in water bodies, depleting oxygen levels and increasing toxicity [8].With these challenges, there is an urgent need to develop new wastewater treatment technologies that are cost-effective, simple, robust, and efficient.

One promising solution is the use of nanomaterial offer significant advantages in wastewater treatment compared to conventional methods. Due to their small size and large surface area, nanomaterial exhibit enhanced adsorption and reactivity, making them highly effective at removing a wide range of contaminants, including heavy metals, organic pollutants, and emerging contaminants like antibiotics. Unlike traditional techniques, which can be time-consuming, costly, and less efficient at removing residuals, nanomaterial can rapidly degrade pollutants and reduce sludge volume. Their magnetic properties also allow for easy separation and recovery, contributing to more sustainable and efficient water

treatment processes. Functionalized nanoparticles also exhibit unique physico-chemical properties, such as size, surface charge, and specific interactions with contaminants in wastewater. Their use can optimize several treatment parameters, and response surface methodology can be employed to evaluate experimental data against computational predictions. However, understanding the toxicity of nanoparticles is essential before applying them on a large scale in wastewater treatment.

Considering the importance of sewage wastewater treatment globally, and to meet the rising water demands, there is pressing need to develop new technologies for cost effective, simple, user-friendly, robust and efficient systems. Heavy metals like mercury, lead, cadmium, arsenic, and chromium (Cr) pose serious risks to human health. Among these, chromium is a particularly hazardous contaminant found in wastewater from industries such as textiles, leather tanning, paints, plastics, metallurgy, and electroplating. Chromium's persistence in the environment, its accumulation in living organisms, and its inability to degrade biologically make it a significant source of pollution. Chromium typically exists in two forms: trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. Of these, Cr(VI) is far more toxic and carcinogenic than Cr(III) because it can easily penetrate cell membranes, leading to harmful effects such as lung cancer, skin irritation, and damage to vital organs. The hexavalent state of chromium can occur in various forms, including hydrogen dichromate (HCr_2O_7^-), chromic acid (H_2CrO_4), chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), hydrogen chromate (HCrO_4^-), tetrachromate ($\text{Cr}_4\text{O}_{12}^{3-}$), and trichromate ($\text{Cr}_3\text{O}_{10}^{2-}$).

According to World Health Organization (WHO) guidelines, the permissible limits for hexavalent and trivalent chromium in drinking water are set at 0.05 mg/L and 5 mg/L, respectively. Trivalent chromium, at lower concentrations, plays an essential role in the metabolism of animals and plants, whereas hexavalent chromium is harmful to various organisms, including animals, plants, and microorganisms. Due to the known toxicity of Cr(VI) to humans, it is crucial to remove it from wastewater. Several methods, such as ion exchange, adsorption, bacterial reduction, and chemical reduction, are frequently used to eliminate Cr(VI)[9-11]. However, many of these approaches are expensive and have low efficiency in removing Cr(VI). To address these limitations, the use of heterogeneous photo catalytic reduction has emerged as an effective alternative for converting Cr(VI) to the less harmful Cr(III). Photocatalysis offers significant advantages, such as utilizing renewable solar energy, being cost-effective, and producing minimal by-products, making it a superior method for chromium removal.

Titanium dioxide (TiO_2) nanoparticles have garnered significant attention as an effective photocatalyst for various environmental applications, such as dye degradation and photo reduction. This popularity is due to the low cost, non-toxicity, enhanced stability, and excellent electrical and optical properties of TiO_2 nanoparticles. They have been successfully employed in various forms, including both pure and heterostructure morphologies, for applications like photocatalytic dye degradation and water splitting. When TiO_2 is irradiated with ultraviolet (UV) light, electrons are generated, which facilitate the

photo reduction of toxic Cr(VI) to the less harmful Cr(III). However, this process is often hindered by slow reaction kinetics. To improve efficiency, the addition of hole scavengers, such as acids, along with the photo catalyst can accelerate the reduction process. Studies have shown that the inclusion of acids like formic acid enhances the reduction of Cr(VI) by lowering the pH and increasing proton concentration, which boosts photocatalytic activity. Despite these improvements, the prolonged conversion time required when using acids limits the effectiveness of conventional batch processes for reducing hexavalent chromium. The photocatalytic reduction was carried out without the addition of any electron or hole scavengers.

2. LITERATURE REVIEW

Water with dissolved and suspended substances discharged from various industrial processes, such as the water released during manufacturing, cleaning, and other commercial activities, is termed industrial wastewater. The nature of the contaminants present in industrial wastewater depends on the type of factory and the industry. Examples of industries that produce wastewater are the mining industry, steel/iron production plants, industrial laundries, power plants, oil and gas fracking plants, metal finishers, and the food/beverage industry. The various contaminants commonly found in industrial water outlets are chemicals, heavy metals, oils, pesticides, silt, pharmaceuticals, and other industrial by-products. In general, it is difficult to treat industrial wastewater, as an individual examination of the set-ups and specific treatment plants are required on an industry-based level. Therefore, to deal with this, on-site filter presses are installed to treat the effluent wastewater [12].

Among a variety of heavy metals, chromium and lead have garnered significant attention due to their detrimental effect on the environment. The possible potential threats to ecosystem by these two metals are as follows: Both trivalent and hexavalent forms of chromium are normally found in wastewater. The hexavalent forms are chromate (CrO_4^{2-}) & dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions. Because of its mutagenic and carcinogenic qualities, the hexavalent chromium ion is believed to be more dangerous to human health, but the trivalent form is very less in toxicity, solubility and mobility and found in soils as oxides, hydroxides, or sulphates [13]. Chromium in the form of chemicals are used in a variety of industrial processes, including leather tanning, chrome ore mining, steel and alloy production, dyes production, glass production, wood preservation, textile production, film & photography. It causes liver damage, lung congestion, oedema, and skin irritation etc.

Out of two oxidation states (+2 and +4), more frequent and reactive type of lead is Pb(II). Apart from its presence in natural sources, anthropogenic sources include electroplating units, explosive production, battery manufacture, printing, finishing, photographic materials, glass & ceramic industries [14]. Lead has major health impacts in living creatures even at very low concentrations. Lead poisoning can

harm the nervous system, reproductive system and kidneys and long-term exposure can cause sterility, abortion, and other problems [15]. Given the importance of heavy metal removal and variety of treatment techniques developed, still research continues to develop a viable, cost effective and green approach methodology for all types of wastewater.

Numerous techniques such as reduction, reverse osmosis, precipitation, flocculation & ion exchange are used to remove these metals from effluents, however their limitation lies on the fact that they are costly, rigorous and generates secondary pollutants that are environmentally unfriendly [16]. Owing to this, a newer and better alternative which is environmentally friendly, of less cost, efficient and renewable has been of choice in recent past for capturing of heavy metals from aqueous solutions [17]. Further few are inappropriate, unavailable, inefficient, ineffective or too costly. Adsorption has currently been demonstrated to be a low-cost and effective way of removing heavy metals from wastewater. Although a variety of materials have been used for adsorption, use of metal oxide nano-particles has gained importance due to inexpensive and readily available in huge amount.

The application of nanoparticles in water treatment offers significant advantages due to their high surface-to-volume ratio, which enhances properties such as reactivity, adsorption capacity, and dissolution activity. Unique features like super Para magnetism, semiconducting capabilities, and quantum confinement further contribute to their effectiveness in treating wastewater. Recent advances include various nanomaterials, such as nanostructured catalytic membranes, nano sorbents, and nano catalysts, used for removing toxic metal ions and organic pollutants from water. Carbon nanotubes (CNTs) have revolutionized water treatment technologies due to their high adsorption capabilities for a range of organic pollutants, including dioxins and pesticides, and their ability to be cross-linked with functionalized polymers for enhanced performance. Additionally, metal and metal oxide nanoparticles, including silver, ferric oxides, and titanium oxides, are widely used for heavy metal removal due to their high surface area and minimal environmental impact.

Studies have demonstrated the efficacy of these nanoparticles in removing metals like arsenate, mercury, and lead from wastewater. Specifically, hexavalent chromium and lead, both highly toxic, pose significant environmental and health risks, necessitating effective removal methods. Traditional techniques such as reduction, reverse osmosis, and ion exchange, while effective, are often costly and environmentally unfriendly. Recent research emphasizes the use of metal oxide nanoparticles for adsorption due to their cost-effectiveness, high efficiency, and minimal environmental impact, addressing the need for sustainable and efficient heavy metal removal from wastewater. Although a variety of materials have been used for adsorption, use of metal oxide nano-particles has gained importance due to inexpensive and readily available in huge amount.

2.1 Review on application of TiO₂ nanoparticles in wastewater treatment

Titanium dioxide nanoparticles have gained significant attention in wastewater treatment because of their photocatalytic properties. Researchers have conducted numerous experiments to explore the effectiveness of TiO₂ nanoparticles in wastewater treatment [18]. The results have been promising, showing that TiO₂ nanoparticles can efficiently degrade various organic pollutants and eliminate bacterial contaminants under UV or visible light irradiation. Further studies have focused on optimizing the synthesis of TiO₂ nanoparticles to enhance their photocatalytic activity and stability. Different methods such as sol-gel, hydrothermal, and sonochemical methods have been explored to enhance the efficiency of TiO₂ nanoparticles in the wastewater treatment applications [19]. In addition to their photocatalytic properties, TiO₂ nanoparticles also exhibit antibacterial properties, making them effective in disinfecting wastewater. This dual functionality makes TiO₂ nanoparticles a versatile and attractive option for addressing water pollution challenges. The application of TiO₂ nanoparticles in wastewater treatment has shown degradation of organic pollutants, removal of unwanted metals and dyes. As the demand for sustainable and efficient wastewater treatment technologies continues to grow, it is expected that TiO₂ nanoparticles will play an increasingly important role in meeting these demands [20]. Further research and development in the field will likely lead to innovative applications and advancements in the utilization of TiO₂ nanoparticles for wastewater treatment [21]. In addition to their photocatalytic properties, TiO₂ nanoparticles also exhibit high surface area and stability, making them suitable for wastewater treatment applications. They are easily immobilized onto different supports, such as membranes or beads, allowing for convenient separation after treatment [22]. Moreover, the low cost and abundance of titanium dioxide make it an attractive option for large-scale wastewater treatment projects. However, challenges such as reusability, recovery of nanoparticles, and potential environmental impacts need to be further addressed and researched.

2.2 Importance of TiO₂ nanoparticles for other hazardous pollutants

Recently, there's been a growing fascination with developing eco-friendly ways to make titanium dioxide nanoparticles (TiO₂). This "green synthesis" approach is a double win, as it's good for the environment and opens doors to exciting applications in many fields. Scientists are investigating several green synthesis techniques, including using extracts from plants, harnessing the power of microorganisms, and even mimicking natural processes. One popular technique involves extracts from everyday plants like tea, neem, or aloe vera. These plant extracts act like double agents with two cool powers: reducing the starting materials and stabilizing the resulting nanoparticles. This natural approach allows for the creation of TiO₂ nanoparticles with custom-designed shapes and properties that are ideal for various applications. Table-1 illustrates the efficacy of TiO₂ nanoparticles as a nano photocatalyst for the removal of various pollutants in millimoles per liter (mmol/L)).

Table 1 Efficacy of TiO₂ nanoparticles as a nano photocatalyst

Nano Photocatalyst	Target Analyte	Initial Concentrations of Pollutant	Efficiency	Abs. Nano photocatalyst	References
TiO ₂	Nitrobenzene	50mmol/L	100%	0.1 g/L	[23]
TiO ₂	Methylorange	30mmol/L	100%	3g/L	[24]
TiO ₂	Rhodamine	125mmol/L	90%	00.1g/100g	[25]
TiO ₂	Parathion	50mmol/L	70%	1 g/L	[26]
TiO ₂	Benzene	45mmol/L	72%	5g	[27]
TiO ₂	Rhodamine b	1.0×10^{-5} M	100%	1.8g/L	[28]
TiO ₂	Toluene	45mmol/L	97%	50 g/L	[29]

Another promising approach is the microorganism-mediated synthesis of TiO₂ nanoparticles. The use of microorganisms presents a sustainable and cost-effective method for synthesizing TiO₂ nanoparticles, with the added advantage of potentially tuning the properties of nanoparticles through, microorganism choice and conditions of growth. Bio-inspired synthesis techniques, mimicking natural processes, have also been investigated for the green synthesis of TiO₂ nanoparticles. These techniques aim to harness the principles observed in biological systems to fabricate TiO₂ nanoparticles with enhanced properties, such as improved stability and reactivity. The review of relevant literature as given at Table 2, provides valuable insights into the various green synthesis techniques for TiO₂ nanoparticles and their potential for sustainable and eco-friendly nanoparticle production. Further research in this area holds great promise for advancing green synthesis methodologies and expanding the applications of TiO₂ nanoparticles in diverse fields.

Table 2 Applications of various nano particle-based systems for the treatment of pollutants in wastewater

Sl. No.	Nanoparticles	Techniques to characterizethe nanoparticles	Contaminants	Parameters studied	Reference
1	Aluminum oxide	SEM	Dunaliellasalinalacells	Morphology, chlorophylla, and carotenoidcontent	[30]
2	Ceriumoxide	SEM	Proteobacteria, unclassified bacteria, Firmicutes, and Actinobacteria Phosphate and nitrate	NaR and NiR, ADKandPPK	[31]
3	Copperoxide	XRD, TEM	Industrial wastewater	Catalytic oxidation,COD	[32]
4	Graphene	TEM	Rhodamine B	Adsorption kinetics,Langmuir isotherm	[33]

5	TiO ₂	Powder XRD, FTIR,DLS, TEM, BET surface area, zeta potential and UV–vis-spectroscopy	Wastewater	Photo degradation	[34]
6	TiO ₂	Powder XRD, FTIR,DLS, TEM, BET surface area, zeta potential, and UV–vis spectroscopy	Dyes	Photocatalysis	[35]
7	TiO ₂	Powder XRD, FTIR, DLS, TEM, BET surface area, zeta potential, and UV–vis spectroscopy	Chromium	Photocatalysis	[36]
8	ZnO	X-ray diffraction and TEM	Bacteria	MIC, MBC	[37]
9	ZnO	UV–visible spectrophotometer, variations in color, pH, and particle size analysis	Bacteria, nitrogen, phosphorus	EPS	[38]
10	Magnetic iron oxide and silicon oxide	FTIR, SEM, and TGA	Cu(II), PB(II)	Sorption efficiency	[39]
11	Iron oxide, silicon oxide, and titanium oxide	DLS, zeta potential, UV–visible spectroscopy, EDX, SEM	Organic content of OMWW	COD	[40]
12	Titanium oxide, magnesium oxide, and aluminum oxide	DLS, zeta potential, UV–visible spectroscopy, EDX, SEM	Cd ²⁺ , Cu ²⁺ , Ni ²⁺ , and Pb ²⁺	Freundlich and Langmuir isotherms, SEM- EDX, SI	[41]
13	Titanium Oxide and gold	DLS, zeta potential, UV-visible spectroscopy, EDX, SEM	Thiocyanate ions, azodyes, 4-chlorophenol		[42]

3. MOTIVATION, OBJECTIVE AND SCOPE OF WORK

3.1 Motivation

Nanotechnology-based pathways, which are being employed for wastewater remediation, are adsorption and bio-sorption, nano-filtration, photocatalysis, disinfection and pathological control, sensing and monitoring and so on. Nanometal oxides are considered more effective adsorbent as compared to activated carbon when removal of heavy metals and radioactive metals are concerned. Additionally, their small size and large surface area offers a small intraparticle diffusion distance which can be compressed without altering their surface area. The sorption process is mainly governed by the complexation between dissolved metals and the oxygenin metal oxides. So it will be an interesting study to find the application of metal oxide nano-particles which was prepared using ultrasonic assisted green synthesis technique, in treating waste water particularly the selected heavy metals.

3.2 Objective & Scope of the Work

The objective of the present work is to assess the performance of green synthesized metal oxide nano-particles as adsorbent for removal of heavy metals from synthetic and industrial waste water. With the above objective, the following study plans are made:

- a) To prepare green synthesized metal oxide nano-particles using plant extract and metal salt solution assisted by ultrasonic technology.
- b) To characterize the metal oxide nano-particles (MONP) by using various techniques such as X-ray diffraction, Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), UV-Visible spectroscopy study and particle size analysis.
- c) To study the optimum solution pH and effective adsorbent dosage for maximum metal ion removal using MONP.
- d) To determine the equilibrium time and use it to other sorption experiments.
- e) To study effect of various adsorption parameters such as metal conc & temperature on removal of heavy metals.
- f) To determine the adsorption capacity of MONP for the removal of metal ions using different adsorption isotherms.
- g) To study the adsorption kinetics mechanism that governs the adsorption process.
- h) To evaluate the thermodynamic parameters, and to find out the nature of the adsorption process
- i) To study the mass transfer parameters and rate-limiting steps.
- j) To examine the desorption of metal ions from MONP by using distinct suitable reagent to regenerate the adsorbent for several cycles.

4. MATERIALS UNDER STUDY

The material undertaken for this research work are metal oxide nonmaterial such

- a) Titanium dioxide and
- b) Aluminium Oxide

4.1 Methodology

The procedure adapted for green synthesis of nanoparticles is given at Fig. 1

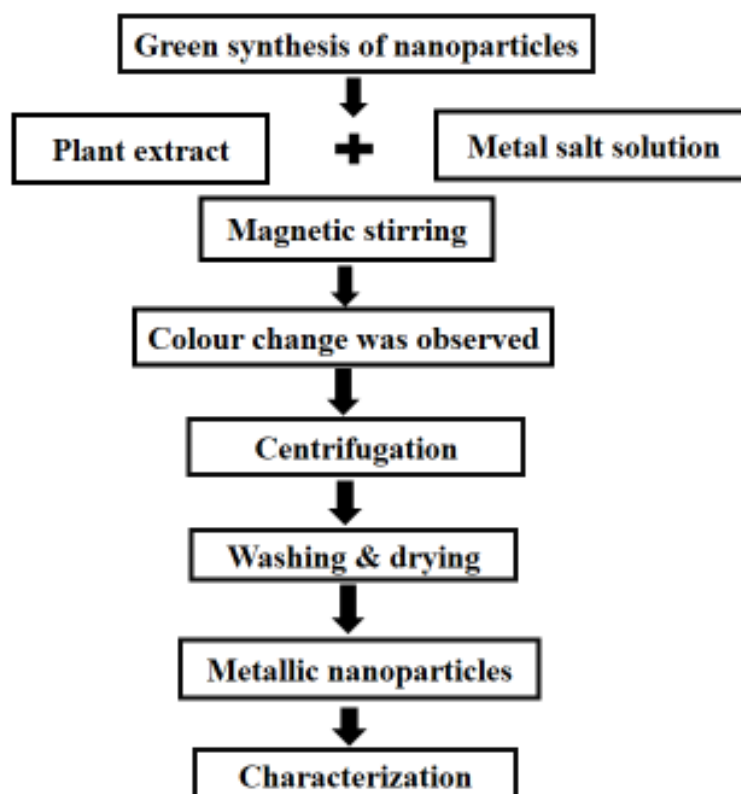


Fig. 1 Flow chart for green synthesis of nano-particles

5. WORK SO FAR DONE

5.1 Synthesis of TiO₂ nanoparticles with leaf extract.

To prepare an aqueous lemongrass extract, fresh lemongrass leaves were collected and thoroughly cleaned with distilled water to remove dust particles. Approximately 20 grams of the washed leaves were boiled in 100 mL of distilled water for 30 minutes at 80°C. After boiling, the mixture was filtered using Whatman filter paper to obtain a clear extract. Sonication played a critical role in synthesizing TiO₂ nanoparticles using the leaf extract. The application of ultrasonic waves during this process enhanced reaction kinetics by improving the mixing and increasing the interaction between reactants. This led to a more uniform particle size distribution while preventing nanoparticle agglomeration, ensuring well-dispersed TiO₂ nanoparticles. Additionally, sonication helped break down the plant cell walls, promoting the release of phytochemicals from the extract, which functioned as natural reducing and stabilizing agents. As a result, the reduction of TiO₂ precursors was accelerated, contributing to nanoparticles with enhanced crystallinity and controlled morphology. Overall, the sonication step improved the synthesis process's efficiency, quality, and consistency. For the green synthesis of TiO₂ nanoparticles, 50 mL of the prepared lemongrass extract was

mixed with 100 mL of a 1M TiO₂ precursor solution. The mixture was stirred continuously at 50°C for 2 hours, during which a colour change indicated the formation of TiO₂ nanoparticles. The solution was then centrifuged at 3500 rpm to isolate the nanoparticles. The resulting precipitate was repeatedly washed with distilled water to remove impurities. Finally, the purified TiO₂ nanoparticles were dried at 80°C for 12 hours to remove residual moisture and obtain stable, dry nanoparticles as shown in Fig.2.

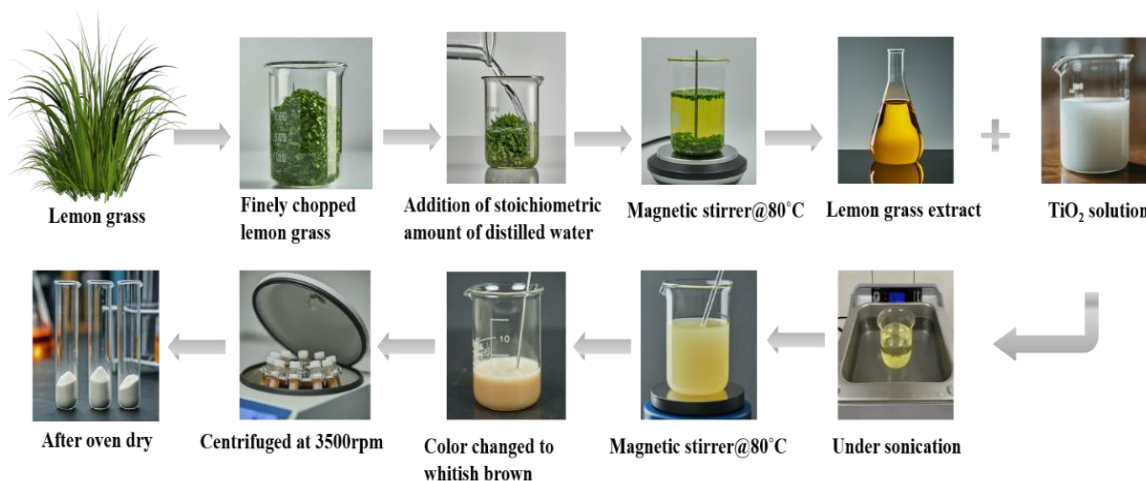


Fig. 2 Preparation of plant extract for synthesis of nanoparticles

5.2 Characterization techniques for TiO₂ nanoparticles

Characterization techniques play a vital role in understanding the physicochemical properties of TiO₂ nanoparticles and optimizing their performance in various applications. Evaluating parameters such as size, shape, surface area, crystallinity, and surface chemistry is essential for a comprehensive understanding of these nanoparticles. The XRD pattern of the green produced TiO₂ nanoparticle was shown in figure 3. With diffraction angles of 27.83°, 36.57°, 39.76°, 41.81°, 44.69°, 55.12°, 57.49°, 63.66°, 65.05°, 70.09°, and 70.85°, respectively, and Miller indices of (1 1 0), (1 0 1), (2 0 0), (1 1 1), (2 2 0), (0 0 2), (3 1 0), (3 0 1), and (1 1 2), the sample verified a high degree of crystallinity. This validates the creation of crystalline TiO₂ with a Tetragonal crystal structure, as seen in the standard JCPDS file no. 01-088-1174, and a lattice parameter of a=b=4.5300Å, c=2.9210Å. The average particle size of biosynthesized TiO₂ nanoparticles was calculated using Scherer's equation.

$$D_{hkl} = \frac{k\lambda}{\beta_{hkl} \cdot \cos\theta_{hkl}} \quad (1)$$

Where D_{hkl} represents the average crystallographic size of the reflected phase, k Scherer constant having value of 0.94, λ is the X-ray wavelength represents the full-width half maximum intensity and θ_{hkl} is the Bragg's angle. It has been demonstrated that the average particle size of TiO₂ nanoparticles generated via biosynthesis is 35.79 nm.

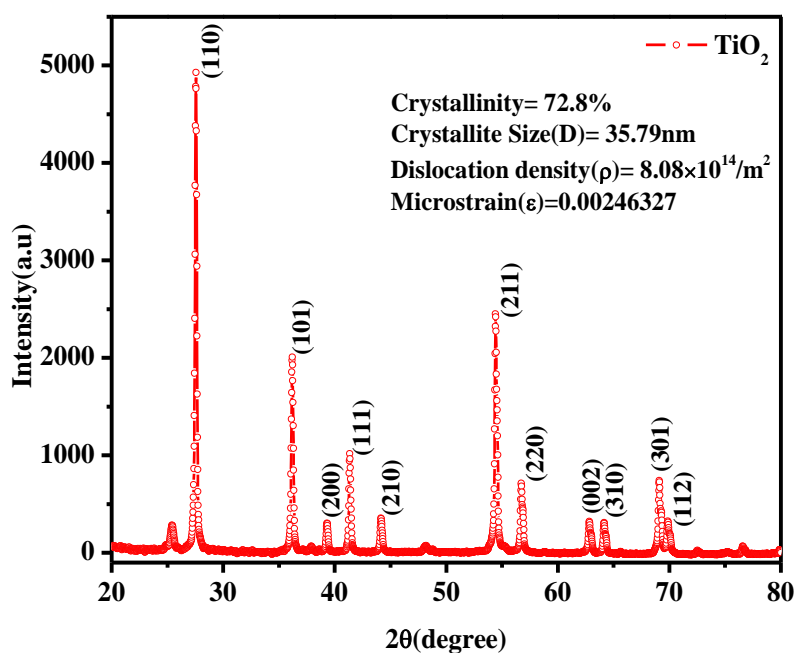


Fig. 3 XRD of TiO₂ nanoparticles

5.3 Understanding of Chromium in wastewater.

The treatment strategy for wastewater is crucial in addressing the presence of hexavalent chromium and ensuring its safe disposal. Hexavalent chromium is a highly toxic compound that can be found in various industries and even in drinking water. Therefore, an effective wastewater treatment process must be implemented to remove hexavalent chromium and prevent its release into the environment. There are two main methods for detecting hexavalent chromium:

- a) **Colorimetric Method:** This is the most common method and is based on the reaction of hexavalent chromium with 1,5-diphenylcarbazide (DPC) to form a violet-colored complex. The intensity of the colour is proportional to the concentration of hexavalent chromium, which can be measured using a spectrophotometer.
- b) **Ion Chromatography (IC) Method:** This method separates different ionic species in a sample based on their affinity for a charged stationary phase. Hexavalent chromium is then detected and quantified using ultraviolet (UV) or inductively coupled plasma (ICP) mass spectrometry (MS).

Both methods have their own advantages and disadvantages. Out of the two methods, colorimetric method is used for the current study.

5.3.1 Colorimetric method:

The colorimetric method is a popular technique for detecting hexavalent chromium (Cr(VI)) due to its simplicity and affordability. Below the detailed explanation of the process:

5.3.2 Sampling and storage:

- **Cleaning of Sampling Bottles:** Thoroughly clean sampling bottles dilute with nitric acid with 6N concentration followed by a final rinse with wastewater. This step ensures that the bottles are free from contaminants that could affect the integrity of the samples.
- **Choice of Containers:** Using chemically resistant glass containers for collect and store water samples. These materials are chosen to prevent any unwanted reactions with the sample.
- **Filtration:** Filter the samples through a 0.45 mm membrane filter as same time of sampling. This step is necessary because of determination of dissolved chromium content, likely to remove any particulate matter that could interfere with the analysis.
- **Analysis Timing:** Analyse the filtered samples within 24 hours of sampling. This timeframe helps ensure the accuracy of the results by minimizing any potential changes in the sample composition over time.
- **Preservation:** Acidify the samples with concentrated nitric acid (2 ml of conc. nitric acid per liter of sample) to bring the pH below 2. Instead of acidifying the samples with concentrated nitric acid, adjust the pH of the samples to 8 or above using 1N sodium hydroxide (NaOH). Then, refrigerate the samples.

By adjusting the pH to 8 or above with in sodium hydroxide and refrigerating the samples, we will be better preserving them for the estimation of dissolved hexavalent chromium. This pH adjustment helps to stabilize the hexavalent chromium species in the sample.

5.3.3 Principle

This method is designed for the specific detection of hexavalent chromium [Cr(VI)] concentration. Hexavalent chromium is quantified through a spectrophotometric process by reacting it with Diphenyl carbazide in an acidic solution. This reaction results in the formation of a red violet coloured complex with an unknown composition. The intensity of this coloured complex conforms to Beer's law and is suitable for spectrophotometric measurements at 540 nm. This technique is effective within the range of 30 to 20,000 µg/L of chromium.

5.3.4 Interference

The reaction involving Diphenyl carbazide exhibits high selectivity for chromium. While hexavalent molybdenum and mercury salts can also produce a colour with the reagent, their colour intensities are notably lower compared to chromium under the specified pH conditions. Concentrations of molybdenum or mercury up to 200 mg/L can be tolerated without causing significant interference. Pentavalent vanadium can cause interference, but concentrations up to 10 times higher than that of chromium are manageable. To

prevent potential interference from permanganate, it is essential to first reduce it with sodium azide. Iron present in concentrations exceeding 1 mg/L may generate a yellow color, although this coloration is typically faint and does not present significant issues, particularly when absorbance is measured spectrophotometrically at 540 nm.

5.3.5 Steps for preparation of Chromium based waste water

1. Spectrophotometer (Spectrophotometer capable of measuring absorbance at 540 nanometre wavelengths with light path of 1cm. This instrument is essential for quantifying the intensity of the colored complex formed during the reaction with Diphenyl carbazide.)
2. pH Meter (A pH meter for accurately measuring the acidity of the solution. Maintaining the specified pH conditions is crucial for the reaction to occur effectively and for minimizing interference from other substances as shown in Fig. 4
3. Standard Volumetric Glassware (Standard volumetric glassware, such as pipettes, burettes, and volumetric flasks, for precise measurement and preparation of solution as shown in Fig. 5. These ensure accuracy and reproducibility in the experiment.)

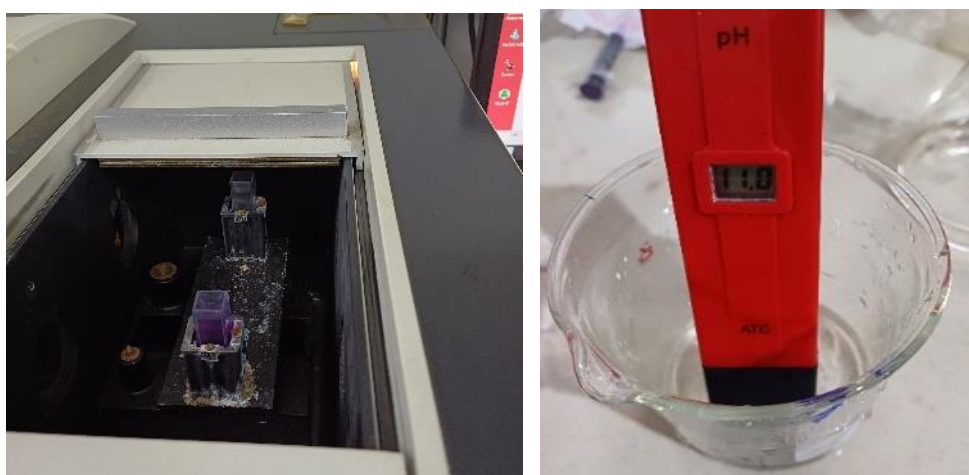


Fig. 4 Spectrophotometer and pH Meter

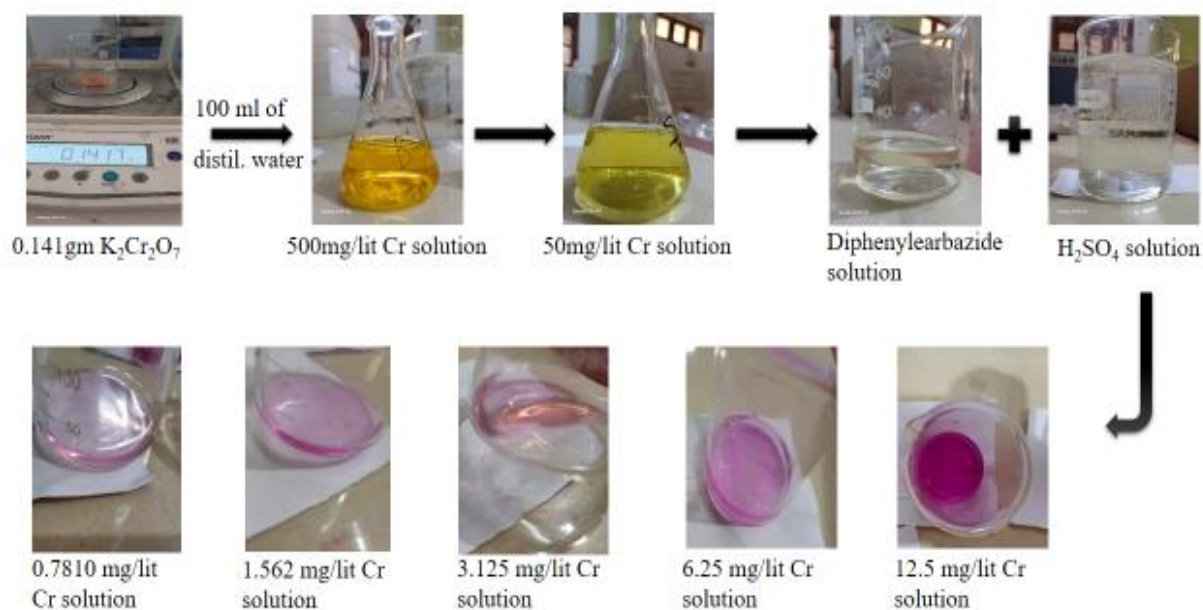


Fig. 5 Laboratory designed chromium based waste water

5. Stock Chromium Solution: Dissolve 141.4 mg of $K_2Cr_2O_7$ in water and dilute to 100 ml. Each millilitre of this solution contains 500 μ g of Cr (500 mg/L).
6. Standard Chromium Solution: Dilute 1 ml of the stock Chromium Solution to 100 ml. Each millilitre of this solution contains 5mg of Cr.
7. Nitric Acid (16N).
8. Sulphuric Acid (36 N).
9. Diphenyl carbazide Solution: Dissolve 250 mg of 1, 5-diphenyl carbazide in 50 ml acetone.

5.4 Procedure for Determination of Chromium

5.4.1 Preparation of calibration curve:

To ensure the precise determination of hexavalent chromium [Cr (VI)] concentrations, standard chromium solutions undergo the same treatment as the samples. This accounts for any potential loss of chromium during the digestion analysis procedures. Standard chromium solutions, ranging from 2 to 20 ml to produce standards for 10 to 100 micrograms of Cr, are transferred into 250 ml beakers or conical flasks. The subsequent treatment mimics that of the samples, including any pretreatment methods employed. Moreover, if cup Ferron treatment is required for the samples, it is also applied to the standards. Following colour development, a portion of each coloured solution is transferred to a 1-cm absorption cell, and absorbance is measured at 540nm, with distilled water serving as a reference. The absorbance readings of the standards are adjusted by subtracting the absorbance for the reagent blank, which is maintained throughout the process. To construct a calibration curve, corrected absorbance values are plotted against

the concentration of chromium. This curve facilitates the determination of chromium concentrations in samples based on their absorbance readings. This rigorous approach ensures accurate and dependable results, compensating for any potential losses or variations in chromium content during analysis.

5.4.2 Determination of Hexavalent Chromium before treatment of TiO_2

From Fig. 6, it can be observed that with increase in absorbance, pollutant concentration (Conc) increases. This indicates that more pollutants are present in the wastewater, leading to higher absorbance at the chosen wavelength as shown in Table 3. From the figure, it is clear that, the Calibration Curve value of 0.9958 refers to the coefficient of determination, commonly denoted as R-squared (R^2). This represents the proportion of the variance in the dependent variable (instrument response) that is predictable from the independent variable (concentration) in a regression model. An R^2 value close to 1 (or 99.5% in this case) indicates that the calibration curve provides an excellent fit to the data, suggesting that most of variability in instrument response can be explained by concentration. Hence, it can be trust for accurately determining substance concentration based on measured instrument responses. It is crucial to note that while a high R-squared value indicates a strong relationship between the concentration and instrument response, it is also important to consider other metrics and factors to ensure the reliability and accuracy of the calibration curve. Additionally, periodic validation and verification of the calibration curve should be conducted to maintain its effectiveness over time. Regular maintenance and quality control procedures will contribute to the ongoing reliability of the quantification process. The high R^2 value implies accurate prediction and suggests reliability and robustness for quantifying analyse concentration based on measured as shown in Fig. 6.

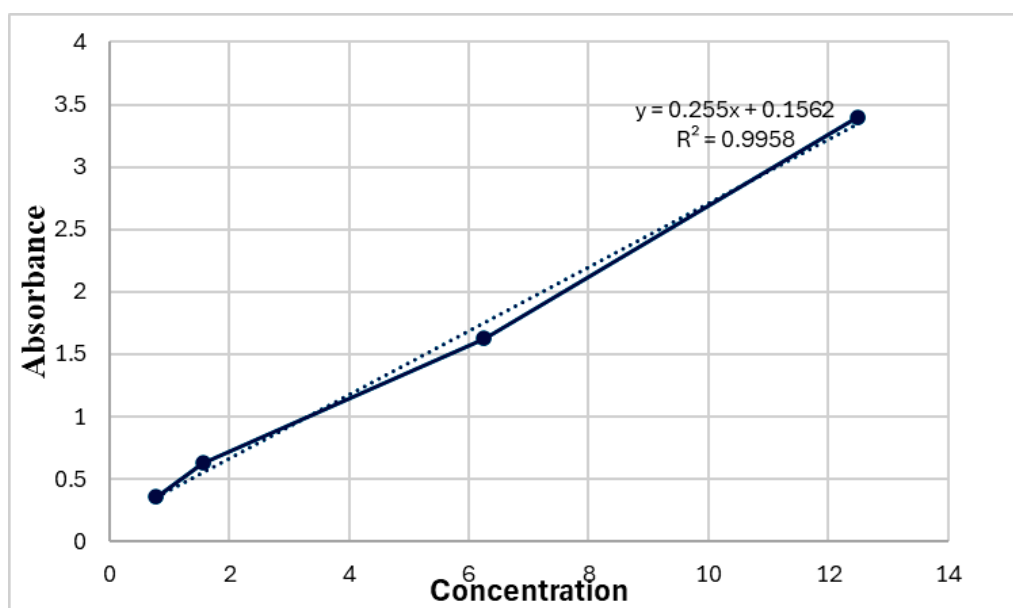


Fig. 6 Absorbance Vs Concentration

Table 3 ABS and Conc. value in wastewater before treatment

Concentration (mg/L)	Absorbance
0.781	0.3549
1.56	0.6261
6.25	1.6252
12.5	3.3979

5.4.3 Determination of Hexavalent Chromium after treatment of TiO₂

Here's a basic procedure for treating TiO₂ in wastewater treatment:

1. **Preparation of TiO₂ Suspension:** Start by preparing a TiO₂ suspension by dispersing TiO₂ nanoparticles or TiO₂-containing material into water. This can be achieved by stirring the TiO₂ powder into water until a homogeneous suspension is formed as shown in Fig.7.
2. **Mixing with Wastewater:** Introduce the TiO₂ suspension into the wastewater to be treated. Ensure thorough mixing to allow the TiO₂ particles to come into contact with the contaminants present in the wastewater.
3. **Stirring and Agitation:** Maintain stirring or agitation of the TiO₂/wastewater mixture to ensure uniform distribution of TiO₂ particles and enhance contact between the catalyst and contaminants.
4. **Reaction Time:** Allow sufficient time for the photocatalytic reaction to occur. The duration of the treatment process may vary depending on factors such as the concentration and nature of contaminants in the wastewater, as well as the intensity of the light source.
5. **Separation of TiO₂:** Once the treatment is complete, separate the TiO₂ particles from the treated wastewater. This can be achieved through filtration, sedimentation, or centrifugation methods.
6. **Disposal or Reuse:** Dispose of the separated TiO₂ particles in accordance with local regulations for hazardous waste disposal. The treated wastewater can be discharged into the environment or reused for non-potable purposes, depending on its quality and local regulations.
7. **Monitoring and Optimization:** intensity, and reaction time may need to be fine-tuned to achieve desired treatment outcomes.

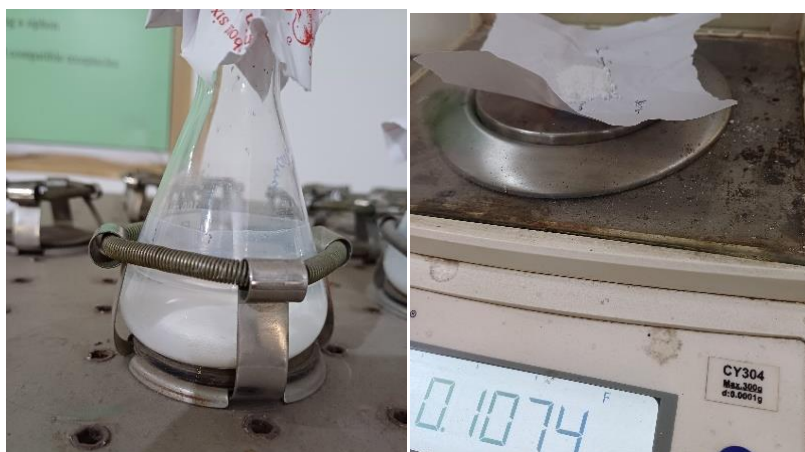


Fig. 7 Addition of TiO₂ with wastewater

5.5 Batch adsorption experiments

Adsorption of Cr (VI) over TiO₂ as an adsorbent were studied through a preliminary batch process to obtain equilibrium data. The Cr (VI) removal studies were conducted by varying initial conc. of Cr (VI) i.e. C₀ (0.781 to 12.5 mg/L). The experiments were carried out in a temperature controlled rotary mechanical shaker using 250 ml flasks containing 100 ml of different Cr (VI) concentrations. Solution of HCl and NaOH were used for adjusting pH to 1±0.3. The study was made keeping other parameters fixed such as adsorbent dose of 100 mg, agitation speed of 150 rpm, temperature as 25±2°C and 120 min contact time. Before taking the reading the samples were filtered through filter paper. The residual conc. of Cr (VI) for all samples after adsorption was determined by spectrophotometer. The amount of Cr (VI) adsorbed per unit mass of the adsorbent was evaluated by using the following equation,

$$\text{Adsorption capacity (mg /g)} (Q_t) = \frac{(C_0 - C_e)V}{M} \quad (2)$$

$$\text{The percentage adsorption (\%)} = \frac{(C_0 - C_e)}{C_e} \times 100 \quad (3)$$

Where, C₀ is the initial conc. of Cr (VI) in mg L⁻¹, C_e is the equilibrium conc. of Cr (VI) in mg L⁻¹, V is the vol. of Cr (VI) solution in lit, M is the weight of adsorbent dose in gm

Table 4 Cr (VI) concentration before and after treatment

Initial Conc. (mg/L)	Absorbance of treated sample	Final Conc. (mg/L)
0.781	0.055	0.121
1.56	0.13	0.324
6.25	0.421	1.62
12.5	1.11	4.1

The final concentration after batch adsorption studies is given below in Table 4. The absorbance for each Cr (VI) concentration, before and after adsorption is plotted in Fig. 8.

Initial concentration is one of the effective factors on adsorption efficiency. The kinetics of adsorption with the adsorbents at different initial concentrations were studied while keeping other parameters constant and the results were found and plotted in Fig. 9. From the figure, it can be observed that chromium removal efficiency decreased with the increase in initial chromium concentration. In case of lower conc. of Cr (VI), the ratio of the initial number of moles of Cr (VI) ions to the existing surface area of adsorbent is high and consequently adsorption becomes independent of initial concentration. However, at higher conc., the available areas of adsorption become less, and hence the % removal of metal ions which depends upon the initial conc., decreases [43]. The maximum percentage removal of Cr (VI) is 84.55%. at initial concentration of 0.781 mg/L.

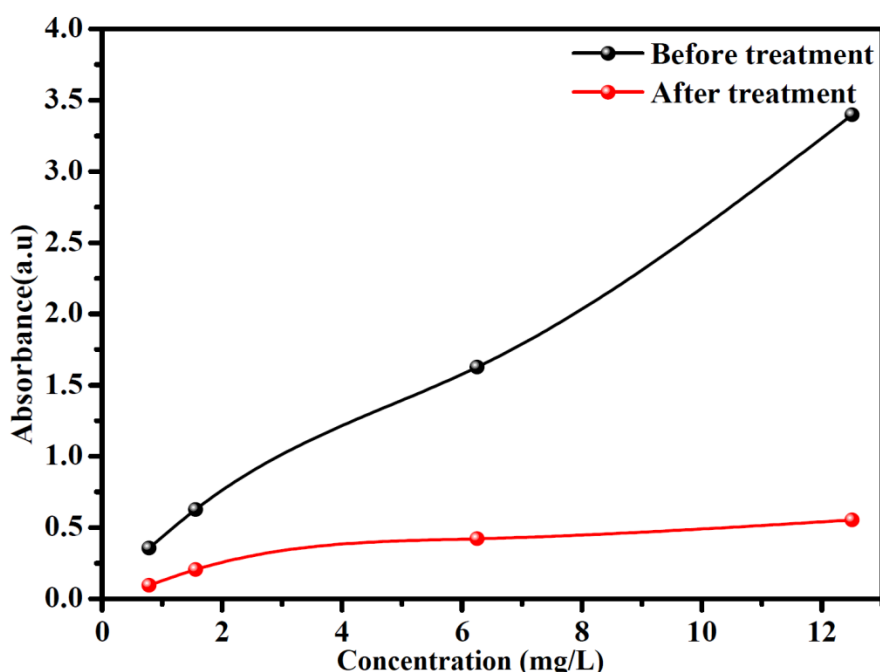


Fig. 8 Comparison of absorption of efficiency of TiO₂ nano particle

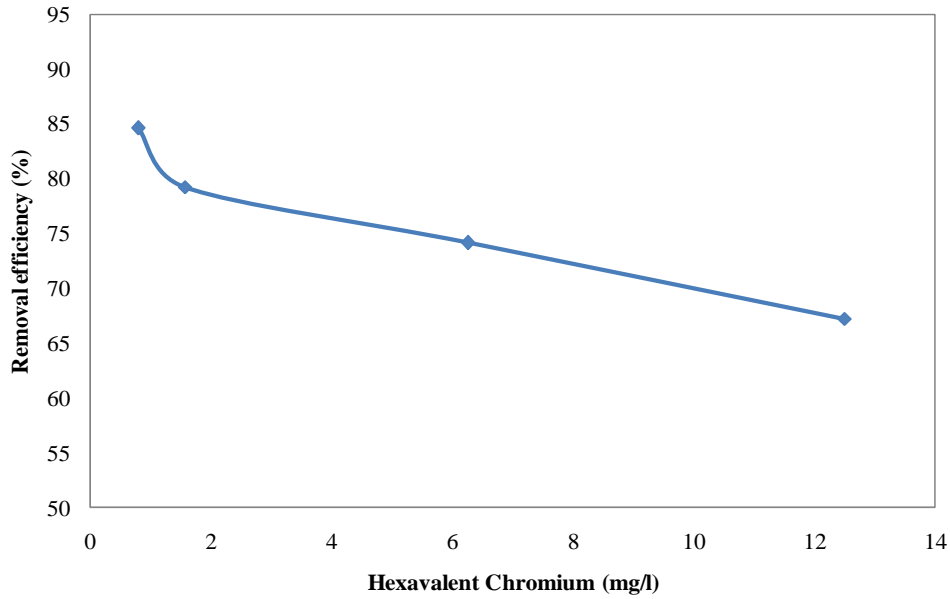


Fig. 9 Effect of adsorbate concentration on removal efficiency chromium (VI)

5.6 Modeling of adsorption isotherms and its studies

For showing the adsorption capacity to simplify possible valuation procedure for a provided application, and to choice of the supreme suitable adsorbent and for the initial calculation of adsorbent dosage necessities the investigational isotherms are most valuable. For the design of the adsorption operations and investigation, the isotherm leads an essential part in the methodical modelling techniques. Langmuir and Freundlich isotherms are often utilized to denote the data of adsorption from the solution [44].

5.6.1 Freundlich Isotherm

The model is generally used to define adsorption over non-homogenous surface. The empirical equation predicts multilayer adsorption due to difference in affinity over adsorption sites. Because of such dissimilarity the isotherm model likewise assumes variation in surface energy of adsorption also [45]. The linearized form of Freundlich isotherm is represented by following mathematical equation:

$$Q_e = K_f (C_e)^{1/n} \Rightarrow \ln (Q_e) = \ln K_f + \frac{1}{n} \ln (C_e) \quad (4)$$

Where, C_e is the equilibrium conc. of adsorbate in bulk solution in mg/L, Q_e defines amount of solute adsorbed per unit weight of adsorbent in mg/g, K_f and n are Freundlich constants representing capacity and intensity of adsorption respectively. Values of K_f and $1/n$ are acquired from intercept and slope of $\log_e Q_e$ vs $\log_e C_e$ linear plot respectively. High value of K_f signifies higher adsorption capacity and value of n between 1 and 10 depict favourable adsorption.

The experimental records were set with Freundlich model, which is presented in Fig. 10. The isotherm diagram showed a linear pattern. Freundlich model constants and R^2 values are calculated and defined in Table 5.

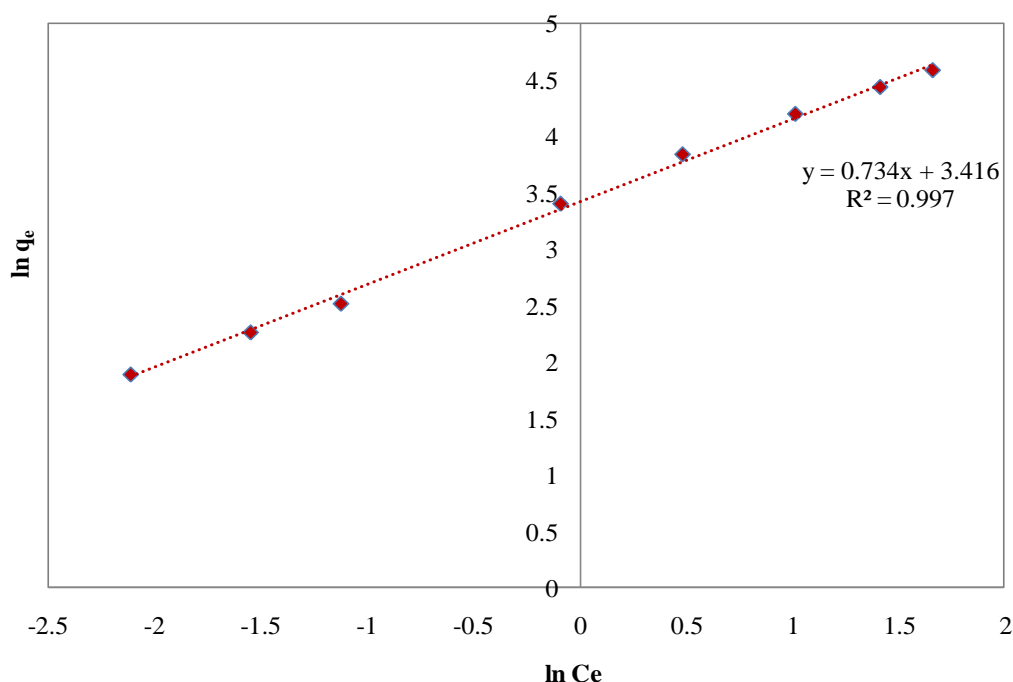


Fig. 10 Freundlich isotherm plots of chromium adsorption on TiO₂

The computed value for R^2 is 0.997 which illustrates an excellence fit and reveal the presence of multilayer adsorption. The values of 'n' was calculated to be 1.36 and showed the favourable heavy metals adsorption [44]. The situation $n > 1$ is most common and may be due to a distribution of surface sites or any factor that cause a decrease in adsorbent-adsorbate interaction with increasing surface density [46]. The values of K_f was found as 30.45.

5.6.2 Langmuir Isotherm

Langmuir adsorption isotherm model assumes that adsorption energies are uniform over homogenous sites (identical sites having equal affinity for adsorbate). It presumes occurrence of monolayer adsorption of adsorbent on the outer surface and considers nil lateral interactions and transmigration amongst adsorbed molecules in the plane of the surface [47]. Once adsorption take place the adsorbate molecules become immobilized, and no adsorption takes place after that. In this model, the energy of adsorption is considered to be constant [48]. The relation between the Cr (VI) uptake capacity Q_e (mg/g) of adsorbent and the residual Cr (VI) concentration C_e (mg/L) at equilibrium is given by

$$Q_e = \frac{Q_0 \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (5)$$

For solid liquid systems, the isotherm is expressed in the linear form as

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (6)$$

$$\text{or } \frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0} \times \frac{1}{C_e} \quad (7)$$

Where, Q_0 is maximum adsorption capacity in mg/g, b is Energy constant = Langmuir Isotherm constant in L/g, this value corresponds to energy of sorption. Values of Q_0 and b were computed by plotting graph between $1/Q_e$ and $1/C_e$.

The experimental records were set with Langmuir model, which is presented in Fig. 11. The isotherm diagram showed a linear pattern. Values of important features like Q_0 and b were evaluated from slope and intercept respectively and are reported in Table 5. The computed value for R^2 is which illustrates a good fit and reveal monolayer type adsorption. The value of Q_0 in (mg/g) and ‘ b ’ was calculated to be 90.91 and 0.61 respectively.

Spontaneity or feasibility can also be determined by evaluating R_L with the help of following equation:

$$R_L = \frac{1}{1+bC_0} \quad (8)$$

Where, b is Langmuir constant and C_0 is the initial concentration of Cr (VI) in mg/L. R_L signifies the separation factor. R_L value between 0 and 1 points to favourable adsorption and if it is greater than or equal to 1 it means adsorption is unfavourable. $R_L=1$ suggests that adsorption is of irreversible nature. The calculated R_L value was equal to 0.098, which substantiates favourable adsorption.

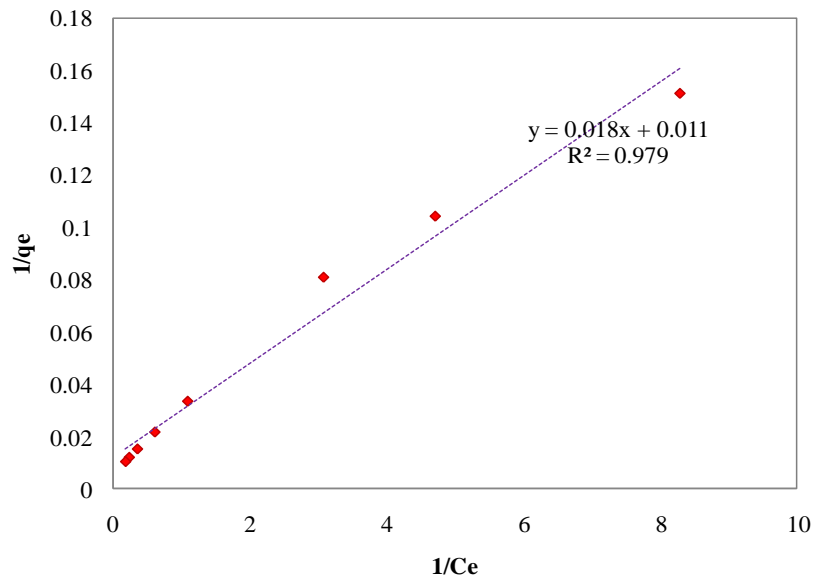


Fig. 11 Langmuir isotherm plots of chromium adsorption on TiO_2

5.6.3 Temkin Isotherm

Temkin isotherm model assumes that decrease in heat of adsorption of adsorbate molecules in the layers is linear rather than logarithmic. Such linear decrease with coverage develops due to interactions between adsorbent and the adsorbate. Adsorption sites with high energies are occupied first [49]. The model also presumes that there is uniform distribution of adsorbate among the layers. It is represented by following equation [50]:

$$Q_e = \frac{RT}{b_t} \ln(K_t \cdot C_e) \text{ or } Q_e = B_1 \ln K_t + B_1 \ln C_e \quad (9)$$

and

$$B_1 = RT/b_t \quad (10)$$

Where, b_t is Temkin isotherm constant, R is the universal gas constant (8.314J/mol/K), T is absolute temperature at 298K, K_t is the equilibrium binding constant (l/mg) corresponding to the maximum binding energy and the constant B_1 is linked to the heat of sorption (KJ/mol).

Binding energies in the range 8-16 KJ/mol point to ion exchange mechanism for adsorption whereas lower values (<8 KJ/mol) predict weak van der Waals interactions supporting physical adsorption. A plot of Q_e versus $\ln(C_e)$ is depicted in Fig. 12. Values for K_t and B_1 were derived from intercept and slope respectively and are quoted in Table 5. Lower binding energy (in present case) hints at occurrence of physical adsorption. The computed value for R^2 is 0.925 which illustrates a good fit. The values of K_t in (L/g) and B_1 in (KJ/mol) was calculated to be 6.57 and 23.92 respectively.

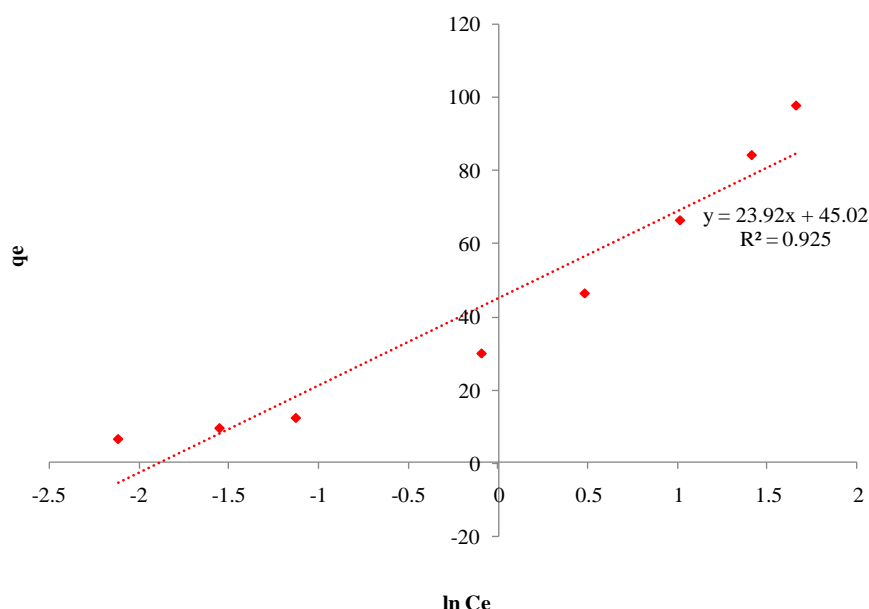


Fig. 12 Temkin isotherm plots of chromium adsorption on TiO₂

Table 5 Adsorption Isotherm Parameters

Model	Parameters	Values
Langmuir	Q_o (mg/g)	90.91
	b ($L\ mg^{-1}$)	0.61
	R_L	0.098
	R^2	0.979
Freundlich	n	1.36
	K_F (mg/g)	30.45
	R^2	0.997
Temkin	k_T (L/g)	6.57
	B_1 (KJ/mol)	23.92
	R^2	0.925

7. IMPORTANT OUTCOMES OF THE PRESENT WORK

Following outcomes has been listed in the present work:

- Importance of ultrasonic as well as green processing of Nanomaterials for wastewater treatment has been assessed.
- The synthesized TiO_2 nano particle drastically changed from 0.1-10 μ m to 35.79nm which is obvious from the XRD-data.
- The calibration curve value of 0.9958 indicates an excellent fit to the data, suggesting that most of variability in instrument response can be explained by concentration. The high R^2 value implies accurate prediction and suggests reliability and robustness for quantifying analyse concentration based on measured.
- .The efficiency of chromium (Cr) removal using TiO_2 in water treatment was found to be 84.55%. This demonstrates the effectiveness of TiO_2 photo catalysis in degrading and removing chromium contaminants from water.

Submitted by
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