Kinetics and Mechanism of Lead Removal from Effluents by Synthesized TiO_2 Nanoparticles Via Sol-Gel method: Adsorption Studies

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ABSTRACT

Water is essential for living organisms, with our bodies containing a significant 60% water content. Water pollution resulting from harmful industrial practices and human activities poses a significant danger to humanity. The release of organic and inorganic substances, pathogens, herbicides, pesticides, drugs, heavy metals, and visible pollutants into water bodies leads to a decline in water quality, causing a reduction in oxygen levels. The toxicity and bioaccumulative properties of heavy metals make them prominent environmental pollutants. Researchers are particularly interested in the adsorption method due to its exceptional ability to eliminate toxic metals, wherein adsorbates bind to the solid surface of adsorbents through physicochemical interactions. In this study, TiO_2 nanoparticles were synthesized via solgel method. These nanoparticles were used to remove lead from contaminated water. Various techniques, including XRD and EDXwere employed to analyze the nanoparticle synthesis. The Atomic Absorption Spectrophotometer was used to measure the removal of Lead before and after adsorption. Key variables like pH, dosage, and contact time were carefully controlled in the experiments. To ensure the findings, statistical analysis were applied to examine all collected data. The ultimate aim was to enhance the efficiency of heavy metal removal and offer valuable insights into the use of chemically synthesized TiO_2 nanoparticles for water purification purposes. This research has the potential to contribute to safer water resources and improved environmental management.

Keywords: Nanotechnology, titanium dioxide nanoparticles, Adsorption, Sol-gel method,kinetic, equilibrium modeling.

1. INTRODUCTION

Water is well known as a universal solvent [1] and a tonic that promotes life. The existence of our planet's biodiversity and the complex food chain that sustains it are both dependent on the water cycle, an essential process. Aquatic pollution [2], which refers to the release of potentially dangerous compounds into aquatic habitats such seas, lakes, rivers, and canals, is a significant problem. These pollutants, which collectively contribute to a reduction in water quality, include pathogens, dyes[3], medicines, chemicals, heavy metals, herbicides, and fungicides. They also comprise organic and inorganic wastes. The effects of these contaminants also include a reduction in water oxygen levels [4], which causes anaerobic decay and the extinction of aquatic life. Furthermore, a variety of disorders are brought on when pollution levels exceed a specific threshold [5]. Oxygen depletion, pH changes, and an increase in microbial population are immediate effects on aquatic life that combined have a negative influence on these sensitive ecosystems[6].

Some heavy metals are discharged into the environment through combustion or as waste in soil or water [7]. Others are utilized in numerous industries for a variety of objectives. These metals may enter the food chain and damage people as well [8]. Wastewater treatment has been hampered by the requirement for clean water, which has prompted the creation of innovative technologies [9]. Pollutants such as dyes, pharmaceuticals, heavy metals[10], and other organic and inorganic chemicals are removed from contaminated water bodies using techniques such flocculation, filtration, degasification, precipitation, photocatalysis, and adsorption [11].

For essential processes including growth, cell metabolism, and organ development, certain heavy metals like copper, nickel, iron, and zinc must be present in living organisms in minute amounts (about 10-15 parts per million). Other heavy metals, such as lead (Pb), mercury (Hg), cadmium (Cd), and related substances, are optional. The environment is exposed to these non-essential heavy metals as a result of both natural and human-made processes [12], such as mining, the production of industrial waste, and vehicle emissions. Living things do not require them in any way. These heavy metals can be absorbed by living things since they readily dissolve in water. Unfortunately, these dangerous metals don't degrade normally and tend to build up inside living things [13].

Lead (Pb) is a smooth-textured silvery-white or grey metal. Although lead is a poor conductor of electricity, it is exceedingly dense, ductile, and malleable. At least as early as 200 BCE, the compound known as the white lead was apparently created as a decorative pigment. The primary lead comes from mine ores, whereas non-essential lead comes from reclaimed products like batteries and lead pipes [14]. Pb-204, Pb-205, Pb-207, and Pb-208 are the most prevalent isotopes of Pb. The radioactive disintegration of thorium(Th) and two separate uranium isotopes gives rise to the last three types of lead. Lead is an old metal that can be found in almost every phase of the inert environment as well as all living systems, and it has a wide range of industrial applications.

A second important source of lead exposure is soil contaminated by residual lead from leaded gasoline and industrial operations [15]. Lead smelters, battery facilities, and automobiles have all emitted hazardous levels of lead-infused pollutants into the atmosphere for many years. This metal is a common environmental toxin, that causes a variety of physiological, biochemical, and behavioral changes. Lead poisoning is a long-standing and serious public health issue that affects people all over the world. It can be ingested, inhaled, or absorbed via the skin. Drinking water has a higher absorption rate of lead than meals. Adults absorb 35 to 50 percent of the lead they consume, while children may absorb more than 50 percent. Lead toxicity causes anemia, colic, neuropathy, nephropathy, sterility, and coma, all of which have been documented since ancient times [16].

The four main methods for treating wastewater are physical, biological, chemical, and sludge-based. Precipitation, coagulation, filtration, reverse osmosis, ion exchange, solvent extraction, sedimentation, adsorption, and electrochemical approaches are just a few of the classic methods that have been used to battle dangerous compounds in polluted water [17]. The high operational costs and poor precision of these techniques, however, frequently render them unsuccessful. Treatment of wastewater with metal levels more than 1000 mg/L can be accomplished using procedures including chemical precipitation and coagulation-flocculation [18].

The adsorption process is preferred by researchers over conventional methods because it is simpler and more affordable [19]. The removal of dangerous metals from home and commercial trash with this technique has a lot of potential for enhancing ecosystem quality.

Through the use of metal oxide, nano-adsorbents, and magnetic adsorbents, emerging innovations in the adsorption method have improved the removal efficiency. Adsorption is the process of liquid molecules attaching to the surface of a solid. Adsorbents solids used for adsorption, are different from adsorbates, which are molecules or ions. Adsorbents can adsorb because of their vast inner surface area [20]. The method of passing a liquid stream over a granular or porous adsorbent medium is often employed for lead separation.Adsorbent materials are often selected depending on process requirements, cost, local availability, and other considerations [21].

Titanium dioxide (TiO_2) nanoparticles play a significant role in the fascinating field of advanced materials and nanotechnology due to their outstanding adaptability and distinctive qualities. These nanoparticles have a wide range of uses, from biomedical engineering to photocatalysis, making them very sought-after in modern scientific study [22] Their exceptional capacity to interact non-covalently with diverse chemicals brings up a world of possibilities for tailored functional enhancements, ultimately leading to better performance in particular utilization circumstances [23].

Stabilizing agents are frequently used in the synthesis of TiO_2 nanoparticles and they play a critical purpose in regulating the nanoparticles' formation and growth [24]. These stabilizing substances interact non-covalently with the nanoparticles, which helps alter their surface characteristics. This alteration is crucial since it increases the nanoparticles' specificity and selectivity in a range of applications. The properties of TiO_2 nanoparticles are shaped by a variety of non-covalent interactions, including hydrogen bonds, van der Waals forces, and electrostatic interactions. This implies that we can modify these nanoparticles to have particular properties for particular needs[6].

In this study, we developed a simple, environmentally benign technique for synthesizing TiO_2 nanoparticles using the sol gel method. Then, characterization of synthesized TiO_2 nanoparticles is done. In the end, the outcomes were enhanced by kinetic and equilibrium modelling.

2. EXPERIMENTAL DETAILS

2.1 Material Synthesis

In first step 100ml isopropanol was poured into a 250ml conical flask and placed on a hot plate, stirred with a magnetic stirrer. 30ml Titanium isopropoxide salt (TIP) was added dropwise slowly within 30 minutes with continuously stirring. In second step, after one hour, 25ml cold distilled water was added slowly with the help of a burette within an hour. To prepare a 3M solution of NaOH, 12 g of NaOH was disintegrated in 100ml refined water. And then, 3 to 4 drops of prepared NaOH solution were added to the Titanium salt solution to provide the basic media. The whole solution was stirred for 6 to 8 hours to produce fine particles. The solution was left in the dark space so that light does not interact with particles. Two layers were formed. With the use of a sucker, the upper layer was removed, and the remaining particles were centrifuged to remove all of the liquid. The particles were then dried in the oven in a petri dish. Particles were calcined in a muffle furnace at 400 for four hours after drying at 120 for four hours. The end result was a white fine powder [25].

2.2BATCH ADSORPTION

In order to create a 1000 ppm stock arrangement of Lead, 1g of Lead sulphate was broken up in 1000 ml of purified water. A 1000ml round-bottom flask was filled with 1g of dissolved lead salt. Adsorption tests were done to find out how well adsorbents like TiO_2 nanoparticles removed lead. The dilution formula ($C_1V_1=C_2V_2$) was used to create working solutions of 50 ppm in 2000 ml of distilled water from stock solutions. 0.1M HCl and 0.1M NaOH were created to modify the pH of working solutions. In order to study the adsorption of lead, various dose rate, concentration, pH, and contact duration parameters were applied to all adsorbent doses of 0.05g. Adsorption tests were carried out by placing 100ml of the working solution with a certain pH in a conical 250ml container. For two hours at a speed of 130 rpm, all of the conical flasks containing samples were placed in an orbital shaker. With dosages of 0.1g, 0.15g, 0.2g, and 0.25g for all adsorbents, the dose rate effect was examined. The pH effect for chromium adsorption was seen at pH 1, 2, 3, and 4. Initial concentrations ranged from 10 ppm to 25 ppm to 50 ppm to 100 ppm to 200 ppm to 400 ppm. The contact time was changed sequentially, at intervals of 0 seconds and 15, 30, 45, 60, 120, 240, 480, 600, 720, 1200, and 1440 minutes.

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF TiO_2 NANOPARTICLES

3.1.1 XRD

The materials generated were pure anatase TiO_2 phase, according to XRD measurements [26], and the crystal structures match the appropriate JCPDS data (JCPDS powder diffraction data card no. 81-84). The diffraction peaks' line broadening indicates that the produced materials are in the nanoscale range. In the reported study the crystalline structure of anatase phase TiO_2 pure is assigned to the XRD peaks at 25.25°, 37.86°, 48.12°, 53.86°, and 55.14°, which correspond to (101), (104), (210), (205), and (211) reflections, respectively [26]. In my research, Peaks at 2θ= 25.52°, 36.14°, 39.12°, 41.35°, 48.15°, 54.32°, and 56.60° correspond to pure anatase phase reflections (102), (105), (211), (204), (116), and (211).The particle size of nanoparticles is related to diffraction broadening peaks. The average crystallite size of TiO_2 nanoparticles was calculated by applying the classical Scherrer formula to the major peaks of diffraction data and taking an average as

$$D = K\,\lambda/\cos\theta \qquad \text{Eq.(1)}$$

where D is the average crystallite size, λ is the X-ray radiation wavelength, K is the Scherrer constant (usually taken as 0.89) for spherical shape, is the full width at half-maximum height (FWHM), and θ is the Bragg diffraction angle.

XRD patterns of nanocomposites comprising 0–20 wt% of nanoparticle content. the number and intensity of characteristic peaks of anatase TiO_2 also increase, while the intensity of the broad hump goes on decreasing, which indicates that the incorporation of TiO_2 nanoparticles in the matrix of char leads to no structural change or new phase formation.

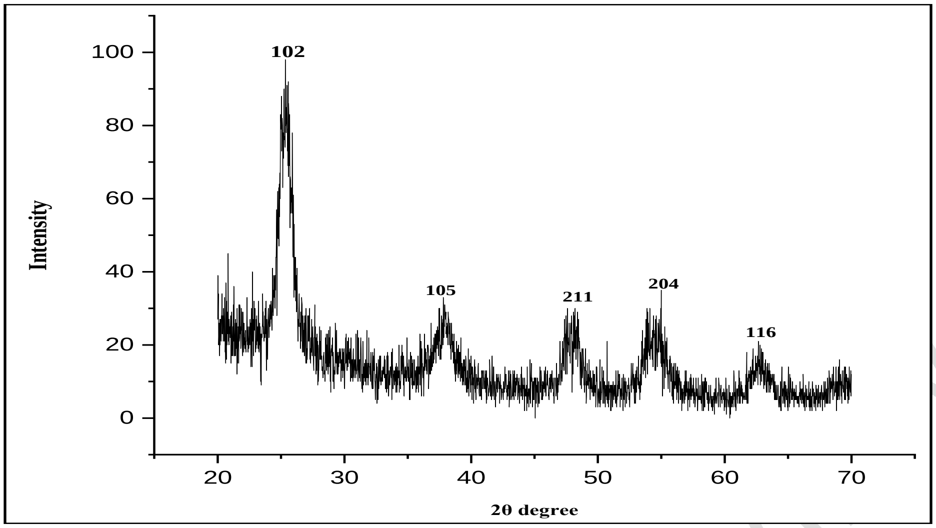

Fig.1XRD pattern f TiO_2 nanoparticles

3.1.2 EDX Analysis

EDX is a standard method for quantifying and identifying elemental compositions in a very minute amount of sample material (even a few cubic µm) [27]. The atoms on the surface are energized by the electron beam in a properly equipped SEM, emitting characteristic wavelengths of X-rays that are specific to the atomic structure of the elements. These X-ray emissions can be examined using an energy dispersive detector (a solid-state device that distinguishes between X-ray energies). This technique, known as EDX (energy dispersive X-ray spectroscopy), is valuable for determining the surface composition of a specimen.

According to the research, the EDX technique was used to determine the elements present in the sample based on their atomic and weight % [28]. Oxygen and Titanium were perhaps the most abundant component in Titanium dioxide nanoparticles, accounting for 41.83 and 45.7 wt% respectively while atomic % were reported as 1.29% and 1.16% respectively. The concentration of Na, C,and Au were reported to be 0.76%, 4.82 and 2.04 wt%, while 0.28, 0.2, 0.76 and 0.69 atomic %, respectively. Cu and Au were considered as an impurity.

An elemental investigation is done by EDX analysis for nanoparticles. The percent of all components in the various composites is recorded. TiO_2 EDX analysis shows the presence of titanium and oxygen.

EDX analysis confirmed that generated nanoparticles are composed of Titanium and oxygen only [29]. No other peak of other element has been found which also confirmed grown nanoparticles are pure TiO_2.

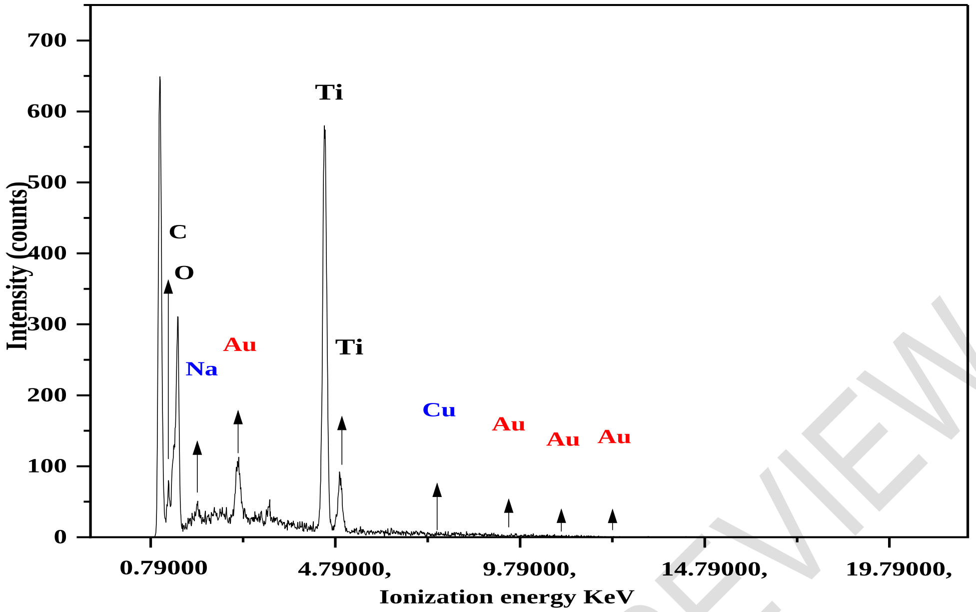

Fig. 2 EDX pattern of TiO_2 Nanoparticles

3.2 CalibrationCurve

Using solutions with different concentrations that were made with distilled water, the calibration curves for lead were shown. Beer Lambert's law validates the lead calibration curves' linear response. According to the Beer-Lambert law principle, the calibration curve has a straight line shape and that a material's absorbance is proportional to its concentration and path length. The following equation for Beer-Lambert's law is given where A is the absorbance, is the molar absorptivity coefficient, c is the analyte concentration, and L is the route length.

$$A=\varepsilon cl \quad \text{Eq.(2)}$$

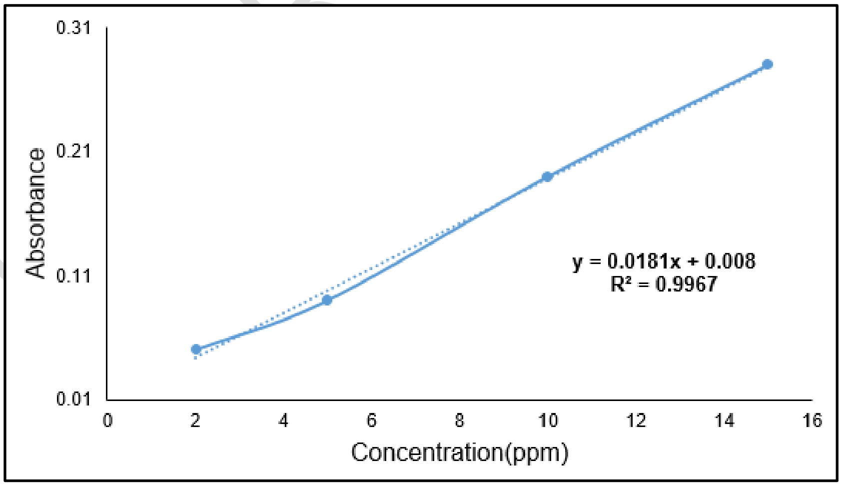

Fig. 3 Optimum Calibration Curve

Table.1 Optimum calibration values for Lead metal

Sr. No.	Concentration (ppm)	Absorbance of Lead

1	2	0.05
2	5	0.09
3	10	0.19
4	15	0.28
5	20	0.36

3.2.1 Effect of pH

The pH of the solution has a big impact on how the adsorption works. Different pH levels may cause the pollutant to behave differently, and functional groups on the adsorbent surface may also do so [30]. As a result, the adsorbent's surface charge density changes, which may interfere with interactions between analyte and adsorbent and reduce adsorption effectiveness. When the pH changes, the groups on the adsorbent's surface undergo protonation and deprotonation [31], which controls the surface charge density. 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 ion generation, have all been reported to be influenced by pH, which is the most significant factor.

In this study, the effect of pH on the adsorption of lead was examined using TiO_2 nanoparticles. At pH=5, the most effective lead removal was seen. At pH 3, TiO_2 nanoparticles removed lead metal with an efficiency of 60.61 percent. Similar to this, it was discovered that the removal efficiency of TiO_2 nanoparticles for lead was 65.1 percent at pH=4 and lower at other pHs. At pH=5, lead levels were discovered to be 73% higher, and at pH=6, lower.

Changes in pH can have an impact on a variety of processes, including the protonation or deprotonation of functional groups [32], the nature of cell surface charge, and the permeability of cell membranes. At different pH values, the adsorption of lead by adsorbent was investigated. Since the cell surface sites were strongly coupled to H+ ions at low pH relative to optimal pH, other cations were inaccessible. However, there was an increase in ligands with negative charges, leading to more cations being bound and a higher pH. Increased negative charge surface of the batteries due to an increase in pH value was beneficial for metal electrochemical adsorption [33]. Based on the data above, pH 5.0 was determined to be the ideal value for lead and was utilized as the starting point for further investigations.

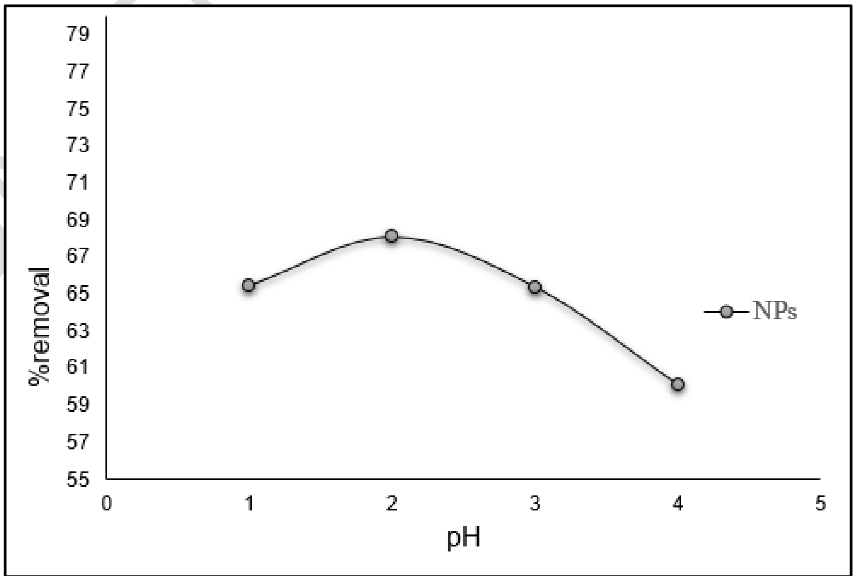

Fig. 4 Effect of pH

Conditions of experiment

Adsorbents = TiO_2 nanoparticles

pH for lead = 5

concentration = 50ppm

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

time = 0 second to 1440 minutes

3.2.2 Effect of adsorbent dosage

The efficiency of dose rate on the elimination of lead metal was tested in this work using TiO_2 nanoparticles [34]. Lead metal's working solution was maintained at a pH of 5, with a starting concentration of 50 ppm. The experiment's removal effectiveness was assessed at dose rates of 0.05g, 0.1g, 0.15g, 0.2g, and 0.25g. The experiment had an initial dosage of 1000 mg/L and was conducted at a temperature of 20°C and an ideal pH of 5. The adsorbent was increased from 0.05 to 0.25 g in volume.

It was shown that the removal effectiveness improved along with the adsorbent dose [35]. This indicates that when the adsorbent dosage rises, more pb+2 adsorption sites become available, increasing removal effectiveness.

TiO_2 nanoparticles demonstrated a clearance rate of lead of 70, 72, 75, 77, and 80 percent at dosages of 0.05, 0.1, 0.15, 0.2, and 0.25 grams respectively. At the highest dosage, the highest percentage of lead elimination was seen. The mechanism underlying this chemistry is a rise in the number of sites on the adsorbent, which led to the highest amount of lead being adsorbed.

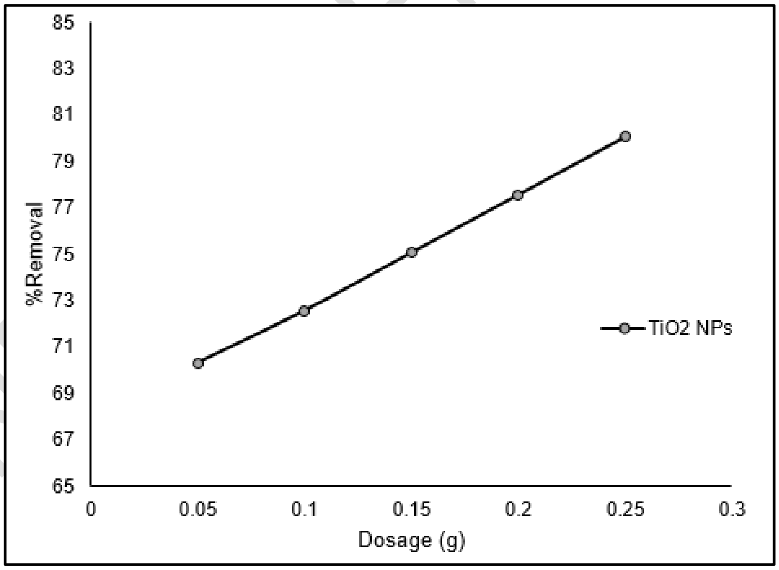

Fig. 5 Effect of Dose rate

3.2.3 Effect of Contact Time

Contact time has the greatest impact on the adsorption parameter. As the amount of contact between the adsorbent and the adsorbate increases, the adsorption rate rises [36]. Kinetic analysis was performed on the surface of TiO_2 nanoparticles. The effect was recorded at 0 seconds, 1, 15, 30, 45, 60, 120, 240, 480, 600, 720, 1200, and 1440 minutes. Adsorption was quicker in the beginning, slowed down over time, and then stayed close to constant after an ideal period or reaching equilibrium [37]. When equilibrium was attained, the metal removal efficiency slowed as the free surface of the nanoparticles reduced due to greater coverage by the bound ions. This may be connected to the speedy absorption of ions onto the huge surface area of nanoparticles as contact duration increased.

At its ideal pH, a workable solution containing 50 ppm and 0.05 g of TiO_2 nanoparticles has been developed. A straight line could be seen on the graph, and gradual rises were noted for up to 10 hours after equilibrium was attained. Most materials were eliminated once equilibrium desorption was observed at the ideal contact time [38]. At 0 seconds, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 120 minutes, 240 minutes, 480 minutes, 600 minutes, 720 minutes, 1200 minutes, and 1440 minutes, respectively, the lead removal was 62, 65, 75, 77, 75, 70, 70, 70, 70, 67, and 65 percent. 77 percent was the highest lead removal rate. The longest removal period was 10 hours, and the removal continued continuously throughout the experimental day.

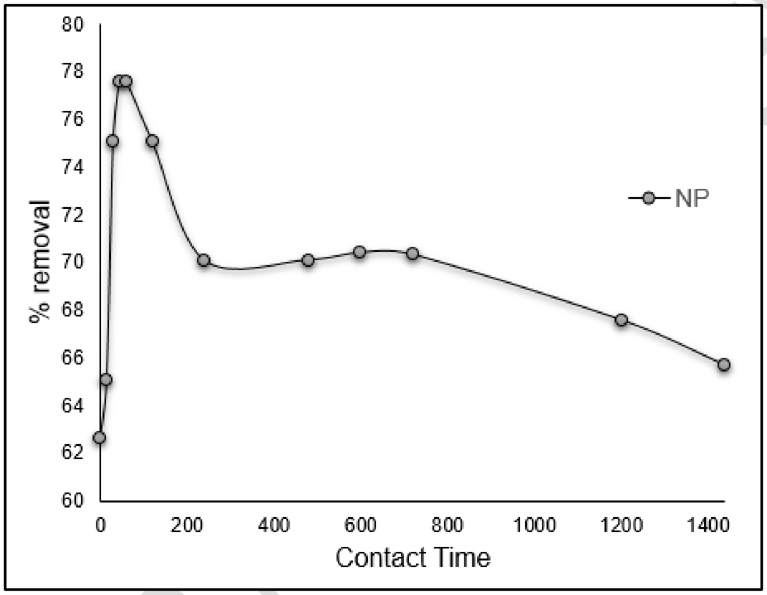

Fig. 6 Effect of Contact Time

3.3 KINETIC MODELS

Kinetic models, Pseudo 1st order and Pseudo 2nd order were applied to observed data to investigate the mechanism of lead adsorption [39].

3.1 Pseudo 1^{St} Order Kinetic Model

In the field of adsorption kinetics,

$$\ln(q_e - q_t) = \log(q_e) - (Kt / 2.303) \quad \text{Eq.(3)}$$

the equation is frequently used, particularly for researching the mechanism of lead adsorption onto a substrate. This equation represents a pseudo-first-order kinetic model, which is frequently used to explain the rate of adsorption over time. In this equation, "ln" stands for the natural logarithm, "q" is the quantity of adsorbate (in this example, lead) adsorbed at equilibrium and at a particular time, "K" is a rate constant, and "t" denotes time. The relationship between the adsorbate amount difference between equilibrium and a specific time and the logarithm of the ratio of the equilibrium adsorbate amount to the adsorption rate constant multiplied by time is effectively expressed by the equation.

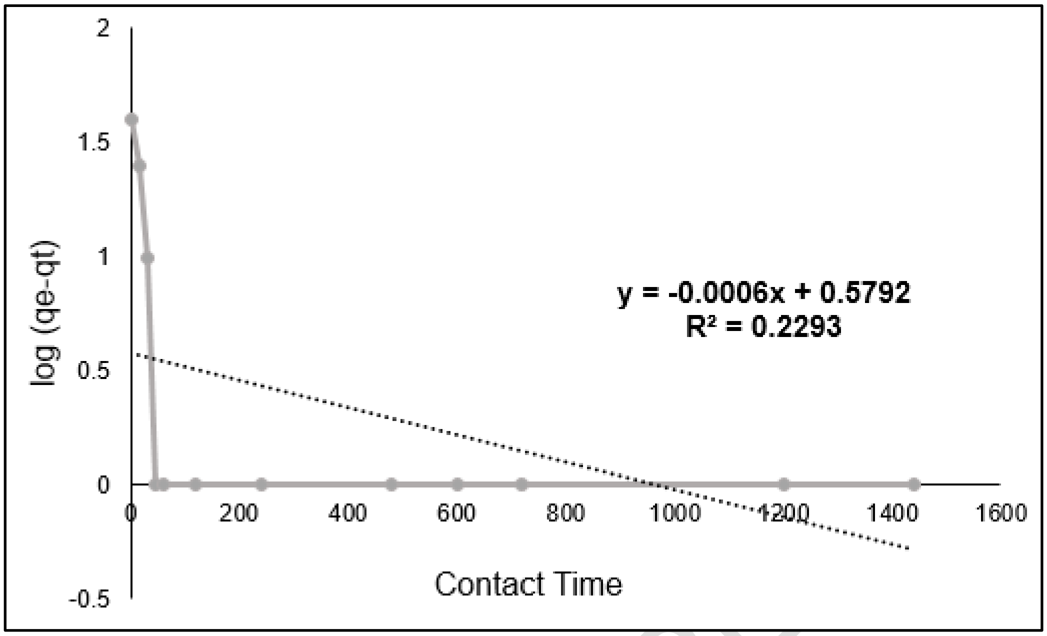

Fig. 7 Pseudo 1st order kinetic model for adsorption of Lead

3.2 Pseudo 2nd Order Kinetic Model

The most popular pseudo-second order equation is written as follows:

$$1/K_2q_2 + 1/q_e = t/qt \qquad \text{Eq.(4)}$$

The adsorption rate constant is represented by the parameter K_2 expressed in units of mass per unit time of adsorbent. In given equation t is time angq represents the amount of adsorbate at equilibrium (q_e).The intercept and slope of the t vs. qt plot can be used to calculate K_2 and q_e. The use of the pseudo-second order kinetics model allows us to better assess the properties of adsorption kinetics. According to this model, the adsorption process is proportional to the square of the number of vacant binding sites.

The results of the study show that both pseudo-first order and second-order rate equations have the potential to explain the behaviors of the studied adsorption systems. When the kinetics data for lead adsorption are analyzed, the correlation coefficient R^2 produced from the second-order rate equation is found to be the best fitting model. Previous studies have primarily used a pseudo-second order kinetic model to investigate the cation sorption process across various adsorbents.

Adsorption kinetics is the study of the pace and mechanisms that regulate surface reactions. This aspect of research provides vital insights and data on the viability of scaling up metal removal from aqueous solutions. Notably, kinetic data from lead removal from aqueous solutions were successfully accommodated inside a second-order kinetic model, providing a noteworthy result.

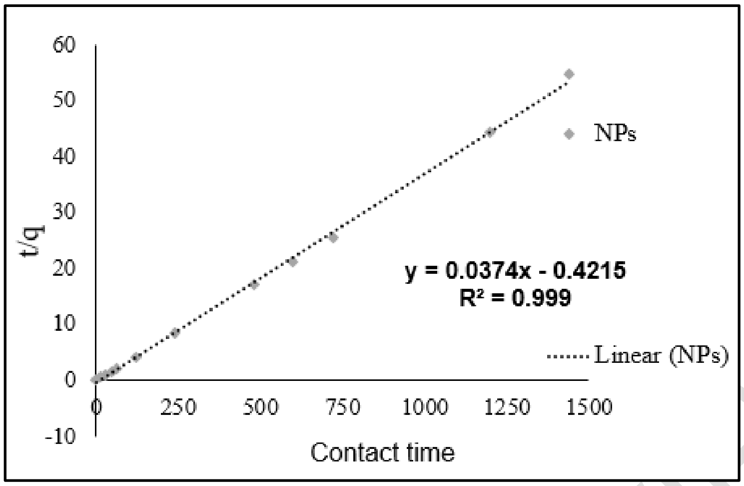

Fig. 8 Pseudo 2st order kinetic model for adsorption of Lead

Table. 2Data for pseudo first and second order for adsorption of Lead onto TiO_2 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**
44.9	16.57	-0.00052	0.47	34.84	0.0020	0.999

4. Conclusion

Water is the second most important requirement for survival after oxygen. Water quality degradation is caused by the presence of many contaminants such as organic and inorganic waste, pathogens, dyes, medicines, chemicals, heavy metals, herbicides, and fungicides. Precipitation, coagulation, filtration, reverse osmosis, ion exchange, solvent extraction, sedimentation, adsorption, and electrochemical techniques have historically been used to reduce water pollution by removing hazardous chemicals. However, these approaches have drawbacks due to their high running costs and limited performance. Adsorption, on the other hand, has gained favor among academics due to its low cost and ease of use.

The primary goal of the study was to create TiO_2 nanoparticles for the purpose of adsorbing lead using an adsorption technique. A series of precisely controlled experiments were carried out utilizing changing concentrations of lead metal solutions to untangle the delicate interplay between TiO_2 nanoparticles and lead metal. These studies were meticulously planned to replicate real-world conditions. To assure the precision and trustworthiness of the results, rigorous steps were followed, with the experiments being run in triplicate. To fully characterize the synthesized materials, a variety of techniques such as EDX and XRD were used. Their pattern suggested a TiO_2 nanoparticle confirmation analysis. Kinetic modelling was used.

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