



Adsorption of Lead from Effluents Using Synthesized ZnO Nanoparticles: A Comprehensive Study for Wastewater Treatment

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Authors' contributions

This work was carried out in collaboration among all authors. Author HA did correspondence, conceptualization, investigation, supervision, writing - review and editing. Author SI did synthesis, characterization and writing. Author MN did coworker, review, editing and writing. Author NKA did writing - review and editing. Author M. Irfan did synthesis, characterization and writing. Author M. Ihsan did review and editing. All authors read and approved the final manuscript.

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ABSTRACT

Water is essential for maintaining life, making up about 60% of the human body. Sadly, water pollution brought on by different industrial processes and human activities seriously jeopardizes our health. The degradation of water quality, which results in lower oxygen levels, is caused by the release of organic and inorganic compounds, pathogens, herbicides, pesticides, medicines, heavy metals, and visual contaminants into water bodies. Heavy metals are among these contaminants that are of special concern to the environment because of their toxicity and bioaccumulative characteristics. The amazing capacity of the adsorption technique to eliminate hazardous metals has attracted the attention of researchers. Through physicochemical interactions, adsorbates are bound to the solid surface of adsorbents using this technique. To eliminate lead from contaminated water, ZnO nanoparticles will create in the current work utilizing the coprecipitation technique for synthesis. To examine the synthesized nanoparticles, number of analytical methods will use, such as UV-Visible spectrum and SEM (Scanning Electron Microscopy). Atomic Absorption Spectrophotometry will also be used to measure the amount of lead removed both before and after the adsorption process. Important factors like pH, dose, and contact time will strictly regulate throughout our research. To confirm the veracity of findings, Kinetic Models will apply. Ultimate goal of this research is to increase the effectiveness of heavy metal removal and offer useful information regarding the usage of chemically produced ZnO nanoparticles for water filtration. This research project has the potential to make a substantial contribution to improving environmental management procedures and protecting our water resources.

Keywords: Nanotechnology; zinc oxide nanoparticles; adsorption; coprecipitation method; kinetic; equilibrium modeling.

1. INTRODUCTION

Water is significant for being a generally useful dissolvable and a tonic that upholds life [1]. The many-sided pecking order that upholds our planet's biodiversity and biodiversity itself are both ward on the water cycle [2], a critical movement. The presentation of possibly unsafe substances into sea-going conditions like oceans, lakes, streams, and waterways [3] is known as amphibian contamination and it is a significant issue. Microbes, colors, prescriptions, synthetic compounds, weighty metals, herbicides, and fungicides are a couple of the toxins that consolidated reason a decrease in water quality [4]. Natural and inorganic squanders are additionally remembered for them. A decline in water oxygen levels is one more impact of these poisons, which brings about anaerobic debasement and the deficiency of oceanic life [5].

The complicated pecking orders that keep up with biodiversity on our planet and the continuation of life rely upon water, which is much of the time referred to as the all inclusive dissolvable [6]. The presence of numerous living things is upheld by the water cycle, a fundamental movement [7]. But since it brings possibly hazardous mixtures into oceanic

conditions like oceans, lakes, waterways, and trenches, sea-going contamination offers a gigantic concern [8]. Microbes, colors, prescriptions, synthetic compounds, weighty metals, herbicides, fungicides, as well as natural and inorganic garbage are only a couple of instances of the tremendous assortment of substances that make up these toxins [9]. Together, these toxins corrupt the oxygen content of the water, which at last causes anaerobic debasement and the peril of sea-going species [10].

Certain weighty metals like copper, nickel, iron, and zinc should be available in small sums (around 10-15 sections for every million) for essential cycles [10] like development, cell digestion, and organ improvement to happen. It isn't expected to utilize extra weighty metals like lead (Pb), mercury (Hg), cadmium (Cd), and related compounds [4]. Both regular and man-made processes, like mining, the making of modern waste, and vehicle discharges, open the climate to these unimportant weighty metals [11]. They are in no way expected by living animals. Since these weighty metals effectively break up in water, living animals can retain them [12]. Tragically, these poisonous metals don't normally breakdown and habitually collect inside living things [13].

A metal with a smooth, gleaming white or dark surface is lead (Pb) [14]. Notwithstanding being a poor electrical transmitter, lead is staggeringly thick, flexible, and pliable [15]. The substance known as the white lead was most likely concocted as a beautiful color to some extent as soon as 200 BCE [16]. While superfluous lead is obtained from reused things like batteries and lead pipes, chief lead is gotten from mining metals [17]. The four most normal isotopes of lead are Pb-204, Pb-205, Pb-207, and Pb-208. The last three lead sorts are made by the radioactive combination of two unique uranium isotopes and thorium (Th) [18]. Pretty much every phase of the latent climate, as well as every single living thing, contain the old metal lead, which has many purposes.

Soil polluted with waiting lead from modern tasks and leaded petroleum is a second huge wellspring of lead openness. For a long time, destructive amounts of lead-injected contaminations [19] have been delivered into the climate by lead smelters, battery fabricating plants, and vehicles. This metal is a commonplace ecological poison that modifies a scope of basic physical processes and biochemical cycles as well as conduct [20]. A tireless and risky general medical condition that influences people from one side of the planet to the other is lead harming. It very well may be consumed by the skin, inhaled, or ingestion [21]. Contrasted with food, drinking water has a higher pace of lead retention [20]. Youngsters might retain over half of the lead they consume, contrasted with grown-ups who ingest 35 to half [22]. Weakness, colic, neuropathy, nephropathy, sterility, and trance like state are symptoms of lead harmfulness.

Soil tainted with waiting lead from modern Physical, natural, substance, and slime based medicines are the four fundamental sorts of wastewater treatment [23]. To battle hurtful substances in debased water, a few conventional methods [24] have included precipitation, coagulation, filtration, switch assimilation, particle trade, dissolvable extraction, sedimentation, adsorption, and electrochemical methodologies. Nonetheless, these techniques normally flop because of their high functional costs and low accuracy. Synthetic precipitation, coagulation-flocculation, and different cycles can be utilized to treat wastewater that contains metal levels more noteworthy than 1000 mg/L [25].

Specialists favor the adsorption strategy to conventional techniques since it is more

straightforward and more affordable [26]. This technique can possibly further develop environment quality by eliminating dangerous metals from private and business trash. Arising headways in the adsorption procedure have expanded evacuation viability using metal oxide, nano-adsorbents, and attractive adsorbents [27]. Adsorption is the interaction through which fluid particles grip to a particle's surface. Adsorbates, which are particles or particles, are unique in relation to adsorbents, which are solids utilized for adsorption [28]. On account of their colossal inside surface region, adsorbents can adsorb. For lead partition, it is normal practice to run a fluid stream over a granular or permeable adsorbent media [29].

Because of their remarkable versatility and novel qualities, Zinc Oxide (ZnO) nanoparticles assume a fundamental part in the captivating field of cutting edge materials and nanotechnology [30]. These nanoparticles are exceptionally pursued in contemporary logical exploration in light of their various applications, which length from photocatalysis to biomedical designing [31]. Their extraordinary capacity to collaborate non-covalently with different particles opens up a large number of chances for modified useful enhancements, which eventually further develop execution in unambiguous use situations [31].

The creation and development of ZnO nanoparticles are firmly constrained by balancing out specialists, which are much of the time used simultaneously [32]. The nanoparticles and these settling specialists communicate non-covalently, changing the surface properties of the nanoparticles [33]. This change is fundamental since it works on the particularity and selectivity of the nanoparticles in various applications. Various non-covalent communications, for example, hydrogen securities, van der Waals powers, and electrostatic cooperations, impact the qualities of ZnO nanoparticles [34]. This recommends that we can change these nanoparticles to give them certain characteristics to suit explicit applications [35].

2. MATERIALS AND MATHODS

2.1 Materials Synthesis

Zinc nitrate and KOH were used as precursors in the direct precipitation approach to create ZnO nanoparticles. In this study, deionized water was used to create the aqueous solutions of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and potassium

hydroxide (KOH), respectively. A white suspension was created after adding the KOH solution slowly while vigorously swirling it into the zinc nitrate solution at room temperature. The white product underwent a centrifugation process at 5000 rpm for 20 min, three washes with distilled water, and a final wash with pure alcohol. The final product was calcined for three hours at 500°C in an air environment [36].

2.2 Batch Adsorption

A 1000 ppm stock arrangement of lead was made by dissolving 1g of lead sulphate in 1000L of clean water. One gram of dissolved lead salt was added to a 1000 ml round-bottom flask. To determine how effectively adsorbents like ZnO nanoparticles absorbed lead, adsorption tests were conducted. From stock solutions, working solutions of 50 ppm in 2000 ml of distilled water were produced using the dilution formula ($C_1V_1=C_2V_2$). To change the pH of working solutions, 0.1M HCl and 0.1M NaOH were made. Different dosage rate, concentration, pH, and contact duration parameters were applied to all adsorbent doses of 0.05g in order to evaluate the adsorption of lead. A conical 250ml container was filled with 100ml of the working solution at a specific pH level to conduct adsorption testing. All the conical flasks containing samples were placed in an orbital shaker and shaken for two hours at a speed of 130 rpm. The dose rate effect was investigated using dosages of 0.1g, 0.15g, 0.2g, and 0.25g for all adsorbents. Lead adsorption was affected by different pH. Initial values were between 10 ppm and 400 ppm, with a range of 25 ppm to 400 ppm. At intervals of 0 seconds, 15, 30, 45, 60, 120, 240, 480, 600, 720,

1200, and 1440 minutes, the contact time was systematically changed.

3. RESULTS AND DISCUSSION

3.1 Characterization of ZnO Nanoparticles

3.1.1 UV visible spectroscopy

The technique of UV-visible spectroscopy is used to examine how a substance absorbs ultraviolet (UV) and visible light [37]. A material will absorb some UV or visible light when it is exposed to it, while the remaining light will pass through [38]. The wavelength of the light and the characteristics of the material both affect how much light is absorbed by it. ZnO nanoparticles have a broad UV absorption band with a peak at about 380 nm in their UV-visible absorption spectra [39]. The electronic transition of ZnO's valence band to its conduction band is what causes this absorption band [40]. The wavelength of the absorption peak can be used to calculate the band gap energy of ZnO [41]. The wavelength of the absorption peak can be used to determine the band gap energy of ZnO, which is typically between 3.3 and 3.5 eV [42]. The size of ZnO nanoparticles can also be determined using the UV-visible absorption spectra [42]. As the size of the nanoparticles decreases, the absorption band widens and gets less strong. This is due to the fact that the surface atoms on the smaller nanoparticles are more exposed to light and have a larger surface-to-volume ratio. ZnO nanoparticles may exhibit additional characteristics in the UV-visible spectrum in addition to the absorption band [43], such as a shoulder at about 250 nm. This shoulder is caused by oxygen vacancies in the ZnO lattice, which absorb light.

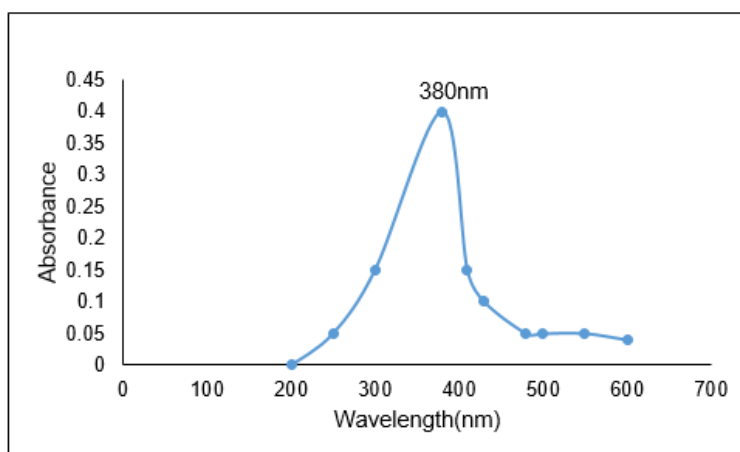


Fig. 1. UV-Vis spectrum of ZnO nanoparticle solution

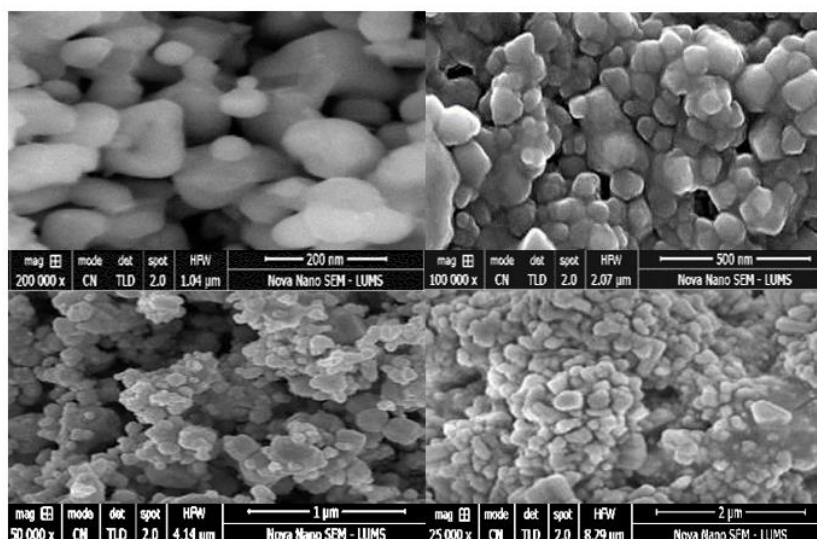


Fig. 2. SEM pictures of ZnO nanoparticles

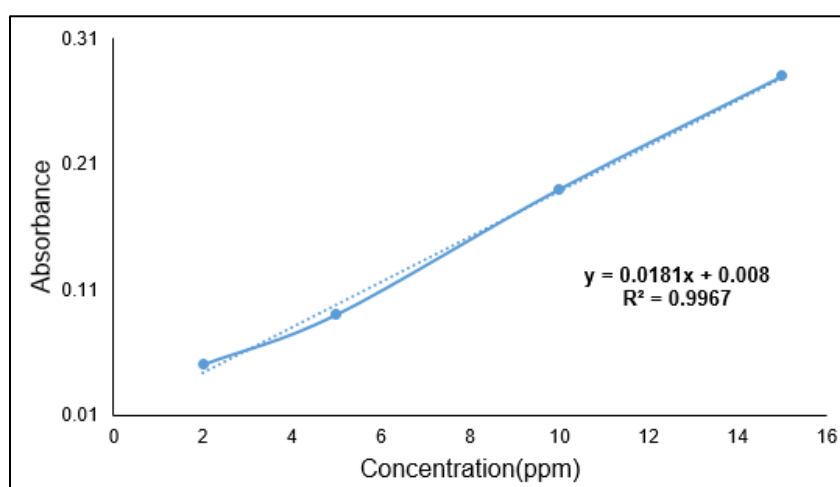


Fig. 3. Optimum calibration curve

3.1.2 SEM analysis of ZnO nanoparticles

Scanning electron microscopy is a method used to examine the surface topography and morphology of materials [44]. It offers details on the size, distribution, and shape of ZnO nanoparticles, allowing for their characterization [45]. A stream of electrons is scanned across the sample's surface in a scanning electron microscope (SEM), and the electrons that reflect back are collected and used to build an image [46]. Agglomerates, fissures, and flaws can all be seen on the image as distinct characteristics on the sample's surface. ZnO nanoparticles have typically been spherical in shape and had an average size of a few nanometers, according to SEM investigation. The characteristics of the

nanoparticles can change as they combine into larger clusters.

3.2 Calibration Curve

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 ($A = \epsilon cl$) is given where A is the absorbance, ϵ is the molar absorptivity coefficient, c is the analyte concentration, and L is the route length.

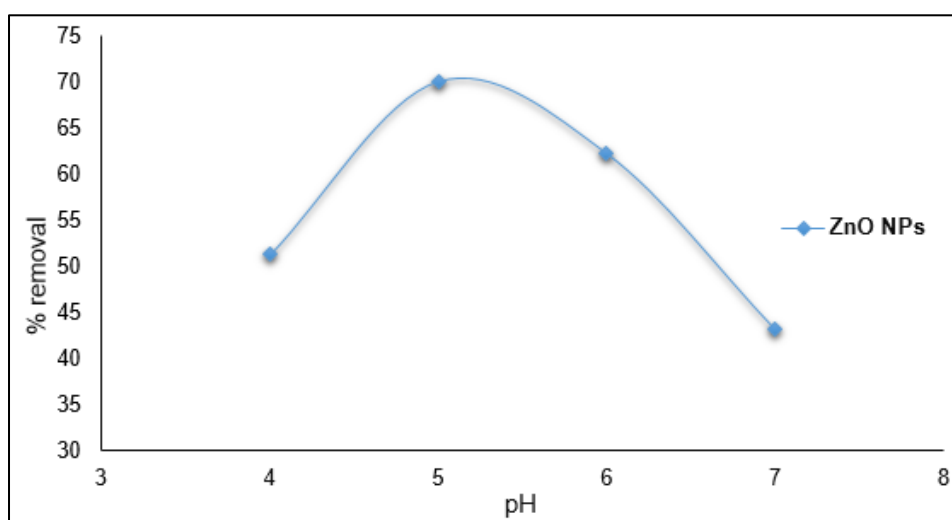


Fig. 4. Effect of pH

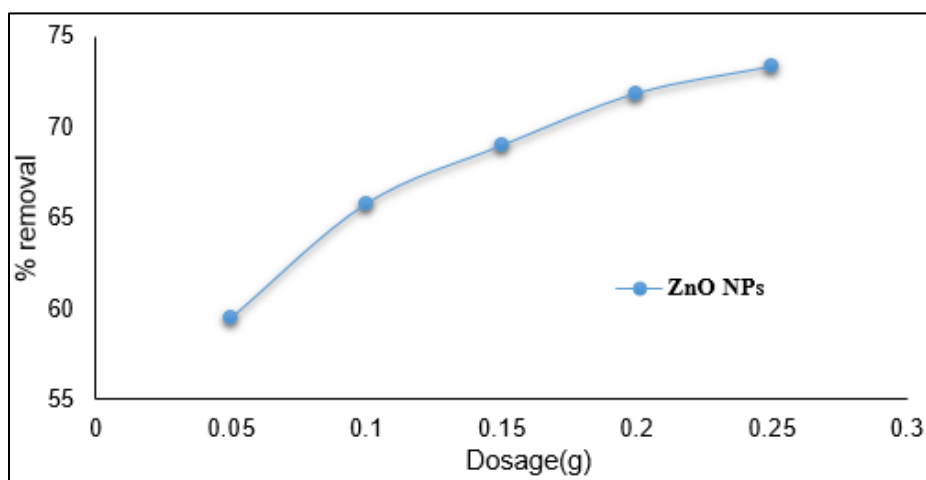


Fig. 5. Effect of dose rate

3.2.1 Effect of pH

The pH of the solution has a significant impact on the adsorption of lead using ZnO nanoparticles. At a lower pH, the surface of the ZnO nanoparticles is positively charged, which repels the negatively charged lead ions. As the pH increases, the surface of the ZnO nanoparticles becomes more negatively charged, which attracts the lead ions. The optimum pH for lead adsorption using ZnO nanoparticles is 5.0. This is because at this pH, the surface of the ZnO nanoparticles has a net negative charge, which is strong enough to attract the lead ions, but not so strong that it repels them. The pH of the solution can also affect the stability of the ZnO nanoparticles. At a lower pH,

the ZnO nanoparticles can be more easily degraded, which can reduce their effectiveness for lead removal. The pH of the solution can also affect the cost of the treatment process. At a lower pH, more chemicals may be needed to adjust the pH

of the solution, which can increase the cost of the treatment process [47].

Conditions of experiment

Adsorbents = ZnO 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

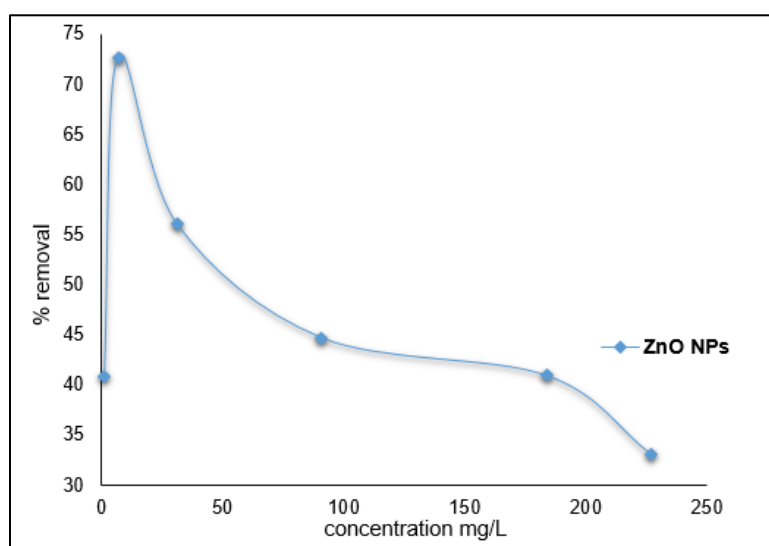


Fig. 6. Effect of contact time

3.2.2 Effect of adsorbent dosage

This study used ZnO nanoparticles to examine how effective dosage rate is at removing lead metal. With an initial concentration of 50 ppm, the pH of the lead metal working solution was kept at 5. The experiment's removal effectiveness was assessed at dose rates of 0.05, 0.1, 0.15, 0.2, and 0.25 g. The experiment was run at an ideal pH of 5, a starting dose of 1000 mg/L, and a temperature of 20°C. The adsorbent was raised from 0.05 to 0.25 g in weight. It was demonstrated that as the adsorbent dose rose, the removal efficiency increased. This shows that when the adsorbent dose rises, more Pb²⁺ adsorption sites open up and the removal rate increases. This shows that when the adsorbent dose rises, more Pb²⁺ adsorption sites open up, increasing the effectiveness of removal. At dosages of 0.05, 0.1, 0.15, 0.2, and 0.25 grammes, ZnO nanoparticles showed a lead removal rate of 70%, 72%, 75%, 77%, and 80%, respectively. At the highest dose, the greatest amount of lead elimination was seen. The rise in the number of sites on the adsorbent, which led to the largest amount of lead being adsorbed, is the underlying chemistry of this phenomenon [47].

3.2.3 Effect of contact time

The adsorption of lead using ZnO nanoparticles is most affected by the contact time. The adsorption rate rises as the time spent in contact between the adsorbent and adsorbate does. This occurs as a result of the nanoparticles' longer

interaction time with the lead ions in the solution. On the adsorption of lead onto ZnO nanoparticles, a kinetic investigation was done. According to the findings, the adsorption rate started out quickly but gradually dropped down. This occurs as a result of the lead ions becoming saturated in the nanoparticles, which leaves less free sites open for adsorption. After 120 minutes of contact time, ZnO nanoparticles were most effective at removing lead from the environment. This happens because there are less free sites available for adsorption and the nanoparticles get saturated with lead ions. After 120 minutes of contact time, ZnO nanoparticles were able to remove lead with their highest possible effectiveness. As a result, equilibrium was reached when the nanoparticles had enough time to interact with the lead ions in the solution. The removal efficiency remained constant after 120 minutes, demonstrating that the system had attained equilibrium. Various experimental factors, such as the concentration of lead ions in the solution, the solution's pH, and its temperature, will affect the ideal contact time for lead removal utilizing ZnO nanoparticles [47].

4. KINETIC MODELS

The pseudo-first-order and pseudo-second-order kinetic models were applied to observed data to investigate the mechanism of lead adsorption.

4.1 Pseudo 1st Order Kinetic Model

The mechanism of lead adsorption onto a substrate is frequently investigated in the area of

adsorption kinetics using the equation $\ln(q_e - q_t) = \ln(q_e) - (Kt / 2.303)$ [48]. The pseudo-first-order kinetic model represented by this equation is a widely used model to describe the rate of adsorption over time. The amount of adsorbate (in this case, lead) adsorbed at equilibrium and at a certain time is denoted by the letters \ln and q in the equation. The rate constant is K , and t stands for time. The link between the amount of adsorbate that differs between equilibrium and a particular time and the logarithm of the ratio of the equilibrium amount of adsorbate to the adsorption rate constant multiplied by time is effectively expressed by the equation. The rate of adsorption is thought to be proportional to the quantity of lead ions that haven't yet been adsorbed, according to the pseudo-first-order kinetic model. This implies that as the quantity of lead ions that have not yet been adsorbed diminishes, the rate of adsorption slows down. The adsorption process' speed can be calculated using the rate constant, K . A faster rate of adsorption is indicated by a greater value of K . A straightforward and user-friendly model that may be used to investigate the mechanism of lead adsorption is the pseudo-first-order kinetic model. It's vital to keep in mind, though, that this model is not always reliable and might not be the ideal one for describing the adsorption of all lead kinds [48].

4.2 Pseudo 2nd Order Kinetic Model

The pseudo-second-order kinetic model might provide a better fit for the data in some

circumstances [49]. According to the pseudo-second-order kinetic model, the amount of lead ions that have yet to be adsorbed squares the rate of adsorption. This indicates that, in contrast to the pseudo-first-order model, the rate of adsorption declines more quickly over time.

The rate of lead adsorption onto ZnO nanoparticles is typically described using the pseudo-second-order kinetic model. According to this concept, the amount of lead ions that have yet to be adsorbed squares the rate of adsorption.

The pseudo-second-order kinetic model's equation is as follows:

$$\text{Where: } t/q_t = 1/k_2 * q_e^2 + t/q_e$$

Lead adsorbed at equilibrium is represented by q_e , where q_e is the equilibrium amount of lead adsorbed and q_t is the time. The pseudo-second-order rate constant is known as k_2 . Data for the lead adsorption onto ZnO nanoparticles have been demonstrated to fit well with the pseudo-second-order kinetic model [50].

Despite being more complicated than the pseudo-first-order kinetic model, the pseudo-second-order kinetic model is typically more accurate [49]. This is because the pseudo-second-order kinetic model accounts for the fact that as the quantity of lead ions that have not yet been adsorbed diminishes over time, the rate of adsorption drops more quickly.

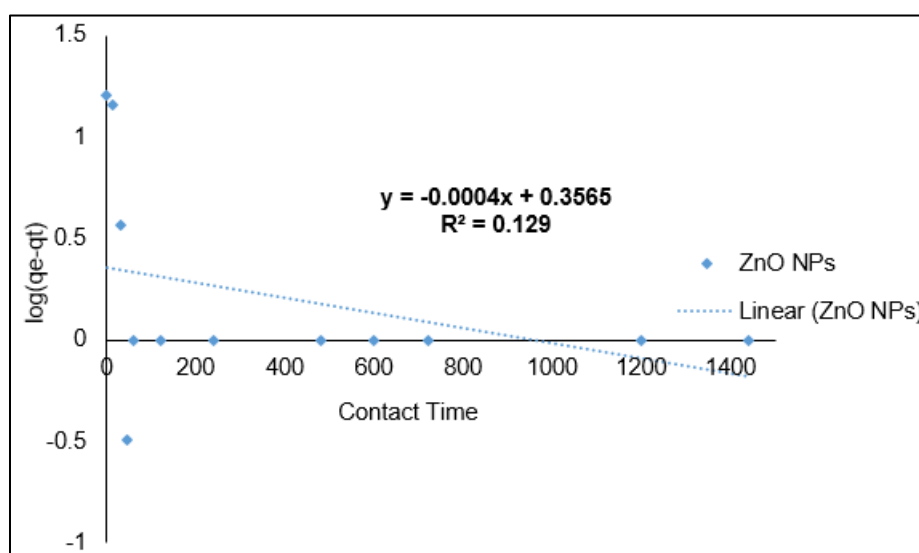


Fig. 7. Pseudo 1st order kinetic model for adsorption of lead

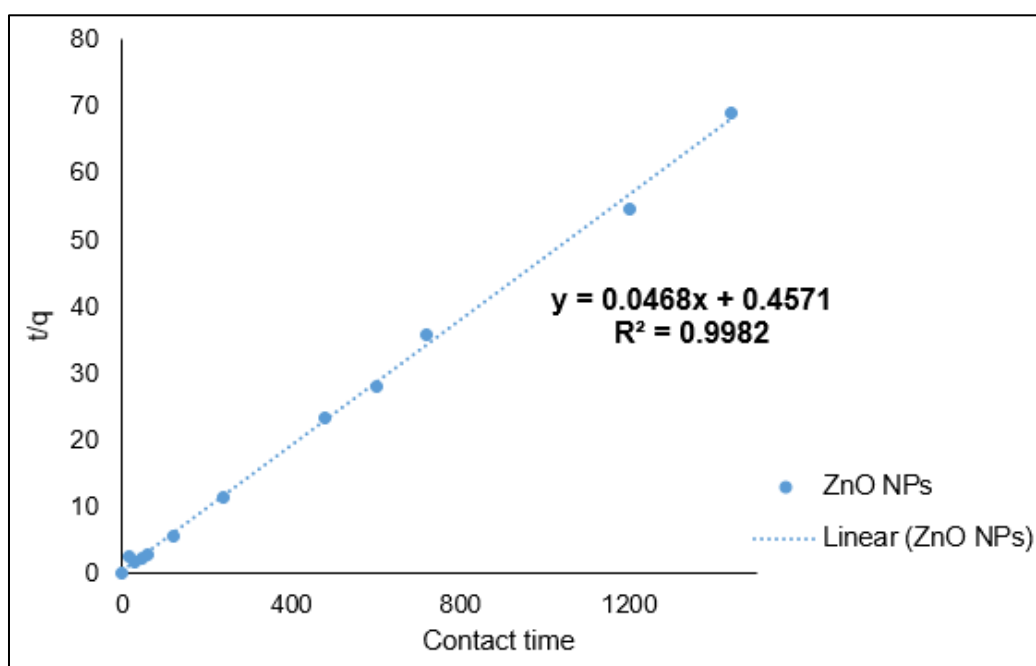


Fig. 8. Pseudo 2st order kinetic model for adsorption of lead

Table 1. Data for pseudo first and second order for adsorption of lead onto ZnO 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
21.93	2.27	0.00017	0.129	21.36	0.00479	0.998

Based on how well the kinetic model fits the experimental data, it should be selected. The mechanism of lead adsorption and the amount of lead that can be adsorbed under various circumstances can both be ascertained using the best fitting model. The data from kinetic studies of the removal of lead and cadmium from aqueous solutions were fitted in a second-order kinetic model in a literature with an appropriate correlation coefficient of 0.99. This shows that the lead adsorption onto ZnO nanoparticles is a good fit for the pseudo-second-order kinetic model [49].

5. 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. Adsorption is a promising technique for removing heavy metals from water. ZnO nanoparticles have been shown to be effective in adsorbing lead from water. A study showed that ZnO nanoparticles were able to remove up to 90% of

lead from water. The adsorption of lead onto ZnO nanoparticles is a physical process that is driven by the electrostatic interaction between the positively charged lead ions and the negatively charged surface of the ZnO nanoparticles. The efficiency of lead removal by ZnO nanoparticles is affected by a number of factors, including pH of the water, the dosage of ZnO nanoparticles, and the contact time. The optimum conditions for lead removal by ZnO nanoparticles will vary depending on the specific application. Kinetic modeling can be used to study the rate of adsorption of lead onto ZnO nanoparticles. This can help to optimize the conditions for lead removal and to predict the amount of lead that can be removed under different conditions. In summary, ZnO nanoparticles are a promising material for the removal of lead from water. Further research is needed to optimize the conditions for lead removal and to develop cost-effective methods for using ZnO nanoparticles in water treatment applications.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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