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Adsorption of heavy metal ions from waste water *via* using the application of metallic oxides

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Abstract

Presently, there is increased attention and focus on addressing issue relevant to heavy metals toxic effects discharge in an aqueous environment. The objective of current research work is to identify most suitable adsorbent among zinc oxide (ZnO), titanium oxide (TiO₂), and aluminum oxide (Al₂O₃), utilized for the efficient removal of lead (Pb²⁺) ions from waste water streams through the adsorption process. In this context, synthetic ZnO demonstrated superior performance in lead uptake, followed by TiO₂ and Al₂O₃. The employed adsorbents were also subjected to characterizations through SEM, EDX-spectra analysis to examine the surface morphology and chemical composition of the adsorbents. The surface and elemental modification ensure maximal adsorption of toxic (Pb²⁺) ions from waste water streams is achieved. To ensure a good adsorption practice of adsorbents for (Pb²⁺) ion, various physiochemical parameters such as solution pH, adsorbent dosage, contact time, initial concentrations and temperature were systematically explored. The optimal conditions for achieving a 100 ppm (Pb²⁺) ion removal efficiency were recorded at pH 7.0, 2.0 g/l of adsorbent dose at 41°C for 120 mins, respectively. Under these optimal conditions, the estimated optimal removal efficiencies for ZnO, TiO₂ and Al₂O₃ were 98.43%, 96.45%, and 85.50%, respectively. Furthermore, adsorption kinetics were explored to remove Pb²⁺ ion and it was observed that the pseudo-second-order provided the best fitted model with a correlation coefficient ($r^2 \geq 0.96$). Based on the data obtained this study confirms that ZnO exhibits higher potential for Pb²⁺ ion uptake on a commercial scale. This potential makes it a valuable candidate for environmental remediation in industrial effluent treatment, addressing the need to purify contaminated water streams.

Keywords: Adsorbent, Heavy metal ion, Metal oxides, Adsorption, Kinetics.

Introduction

Heavy metal ions removal from industrial waste water stream in a systematic manner is a prime issue of discussion among the world leaders. Heavy metal ions accumulation in an unregulated manner in environment can create toxicity and disturb ecosystem, henceforth there is a need to find an effective method to resolve the issue of metal ions disposal from industrial effluents (Naidu et al. 2019) [1]. Otherwise, the toxic heavy metal ions deposition in air, water (Ghorani-Azam et al., 2016; Luo et al., 2020), soil systems can affect the food chain supply (Khan et al. 2013) as well as the normal functioning of human system (Jaishankar et al., 2014) [2-5]. The most commonly known heavy metals including arsenic, cadmium, chromium, copper, lead, nickel and zinc in waste water streams, all of which have deleterious effect on human health and their environment (Mood et al. 2021) [6]. Of these accumulated metal ions, Lead ions (Pb^{2+}) are one of the toxic metal ions to human and aquatic life when present in a huge amount in water streams (Ahmad et al. 2009) [7]. The presence of Pb^{2+} ions in drinking water above the tolerable limit (5 ng/mL) may cause serious detrimental health problems in humans such as anemia, encephalopathy, liver and kidney disorders. Thus the development of sustainable based technologies have gained attention in recent years are actual remedy to remove the dangerous heavy metal pollutants. Although, several sustainable approaches including chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption has been strongly recommended to remove heavy-metal ions from water/wastewater stream.

Adsorption is one of the most common technique to remove heavy-metal ions due to simplicity and high efficiency nature, as well as the ease of use of a wide range of adsorbents. Based on the adsorption phenomenon several nano-sized nano-materials with greater surface area to volume ratio and simplicity nature can modify their surface functionality characteristics of metal based nano-materials is a matter of fact that have been developed in recent decades. Nano-sized metal oxides including ferric oxides, aluminium oxides, magnesium oxides, zinc oxides, manganese oxides and cerium oxides are considered as the well-known and with tremendous property of extracting adsorbing heavy metal ions from aqueous waste systems.

Zinc oxide nano-materials (ZnO-NPs) are extensively explored as highly efficient adsorbent and lesser toxic material than any other metal oxides owing to have good catalytic power, resistive to adverse photochemical events, eco-friendly and biocompatibility in nature (Salahuddin, et al. 2015; Ruszkiewicz et al. 2017). On the other hand, ZnO-NPs have significant anti-bacterial characteristics against Gram-positive and Gram-negative bacteria, which may be a stringent antifouling mechanism in absorbent containing media (Siddiqi et al. 2018) [8-11]. However, In

recent decades few reports concerning with ZnO-NPs are available and have focused on the removal of toxic inorganic pollutants such as Cu^{2+} , Pb^{2+} and Cd^{2+} from industrial waste water.

Additionally, In this work the potential use of zinc oxide (ZnO), titanium oxide (TiO_2) and aluminium oxide (Al_2O_3)-NPs as a nano-adsorbent for inorganic pollutants removal, particularly lead metal ions have been investigated. These heavy metal ions are often discharge in water systems through various industrial processes such as mining, ceramic glass, plating, coating, posing a significant health risk to human beings. Consequently the research focuses on assessing the adsorption capacity of metal oxide based nano-materials and removal efficiency for prominently found lead (Pb^{2+}) ions in waste water. Furthermore, this study delves into effects of different physical and chemical parameters including pH, adsorbent dose, contact time, initial concentrations and temperature on batch adsorption experiment.

2. Materials and Methods

2.1 Experimental methods

An extra pure (~99%) chemical designated as lead nitrate [$\text{Pb}(\text{NO}_3)_2$], manufactured by Merck Pvt. Ltd., India, was intend to develop the contaminated aqueous solution.

A stock solution of 1000ppm was prepared by mixing 1.58g of lead nitrate in 1L deionized water containing 10% (v/v) hydrochloric acid (HCl) to facilitate avoidance the lead (Pb^{2+}) ions precipitation on account of hydrolysis. In addition, the standard working solution of lead (Pb^{2+}) ions was prepared from stock solution and to adjust concentration in between 50 and 150mg/L. The pH of experimental solution was adjusted by adding either sodium hydroxide NaOH or HCl solutions.

The powered zinc oxide (Analytical grade, ZnO) (99% purest form), titanium dioxide (TiO_2) (98% extra pure) and active aluminum oxide (Al_2O_3) were procured from Merck India Pvt. Ltd. All metal oxides were treated as adsorbents for further studies. The synthetic nano-materials were analyzed morphologically before and after adsorption by means of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) techniques. As per standard protocols prescribed earlier by Rezaei et al. (2022) who revealed the point of zero charge calibration for each of the three adsorbents and it was demonstrated with the help of the pH drift method[12]. Fig.1 had shows noteworthy pH calibration, which was 7.3, 7.1 and 9.0 for ZnO, TiO_2 and Al_2O_3 , respectively.

The batch-wise adsorption procedure is sub-divided into several sets, where; each set computes a particular parameter that affects the adsorption behavior and estimates optimal value among the tested range. In this work, pH of the solution, adsorbent dose, contact time, initial concentration of Pb^{2+} and temperature were undertaken physio-chemical parameters. The pH influence on the adsorption behavior of Pb^{2+} ion requires addition of 0.1M of nitric acid (HNO_3) or NaOH into aqueous solution by adjusting the solution pH 3,5,7 and 9. The tested range of adsorbent dosage

was varied to 0.01 and 0.05g. The effect of contact time was investigated, its value varied from 5 to 120 mins.

The impact of the initial concentration of lead ions is in between 50ppm and 150ppm and the temperature effect was studied between 18°C and 41°C. For accurate measurement of adsorption capacity (Q_{eq}), the aqueous solution was shaken until and unless solution achieved equilibrium state. Afterwards, each set undergone to fractionation steps; where centrifuge and filtration *via* using the Whatmann no: 45 filter paper are included and to analyze the sample qualitatively with the help of model Ultima 2-JY Plasma; inductively coupled plasma (ICP) spectrometry. ICP is used to calibrate accurately the actual lead concentration in contaminated water samples as per the guidelines of Environmental Protection Agency (EPA-US) and follow up EPA standard methods[13]. The adsorption percentage and the capacity of adsorption of adsorbents can be calibrated as per the given Equation (1) and Equation (2), respectively, Cooney, (1999)[14]:

$$Q_{eq} \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_o - C_{eq})V}{m} \text{EQ. (1)}$$

$$(\text{Adsorption } \%) = \frac{(C_o - C_{eq})}{C_o} \times 100\% \text{EQ. (2)}$$

Whereas; Q_{eq} is the mass of metal ions adsorbed per unit weight of the adsorbent at equilibrium stage (mg adsorbate/g adsorbent), C_o is the initial concentration of the metal ions (mg/L), C_{eq} is the equilibrium concentration of the metal ion (mg/L), V is the volume of the metal ion solution (mL), and m is the mass of the adsorbent (mg).

3. Results and Discussions

3.1 Morphological and Chemical Composition analysis of the Adsorbents

The morphology of the adsorbents surface was tested microscopically *via* using the SEM analytical instrument, where SEM images discover peculiar modifications on the surface of the adsorbents before and after the adsorption process, as it is display in Fig 1(a)-1(f). Shown SEM images figures 1(a) and 1(c) displayed the both ZnO and TiO₂ adsorbent changes as it show hard and uneven surfaces with spongy openings before the adsorption process. While; highlighted SEM images 1(e) of Al₂O₃, display the solid and smoothen surfaces with few porous openings. This kind of unusual behavior revealed that the Al₂O₃ had low removal efficiency for Pb²⁺ ions compare to ZnO and TiO₂. Figures 1(b), 1(d) and 1(f)) indicate the porous openings on ZnO, TiO₂ and Al₂O₃ surface, packed with lead ions. The ZnO, TiO₂ and Al₂O₃ morphology conformity was compared before and after uptake of Pb²⁺ ion at different magnification scales (25000X and 75000X); which examined the clear cut change in the morphology and underline the adsorption process.

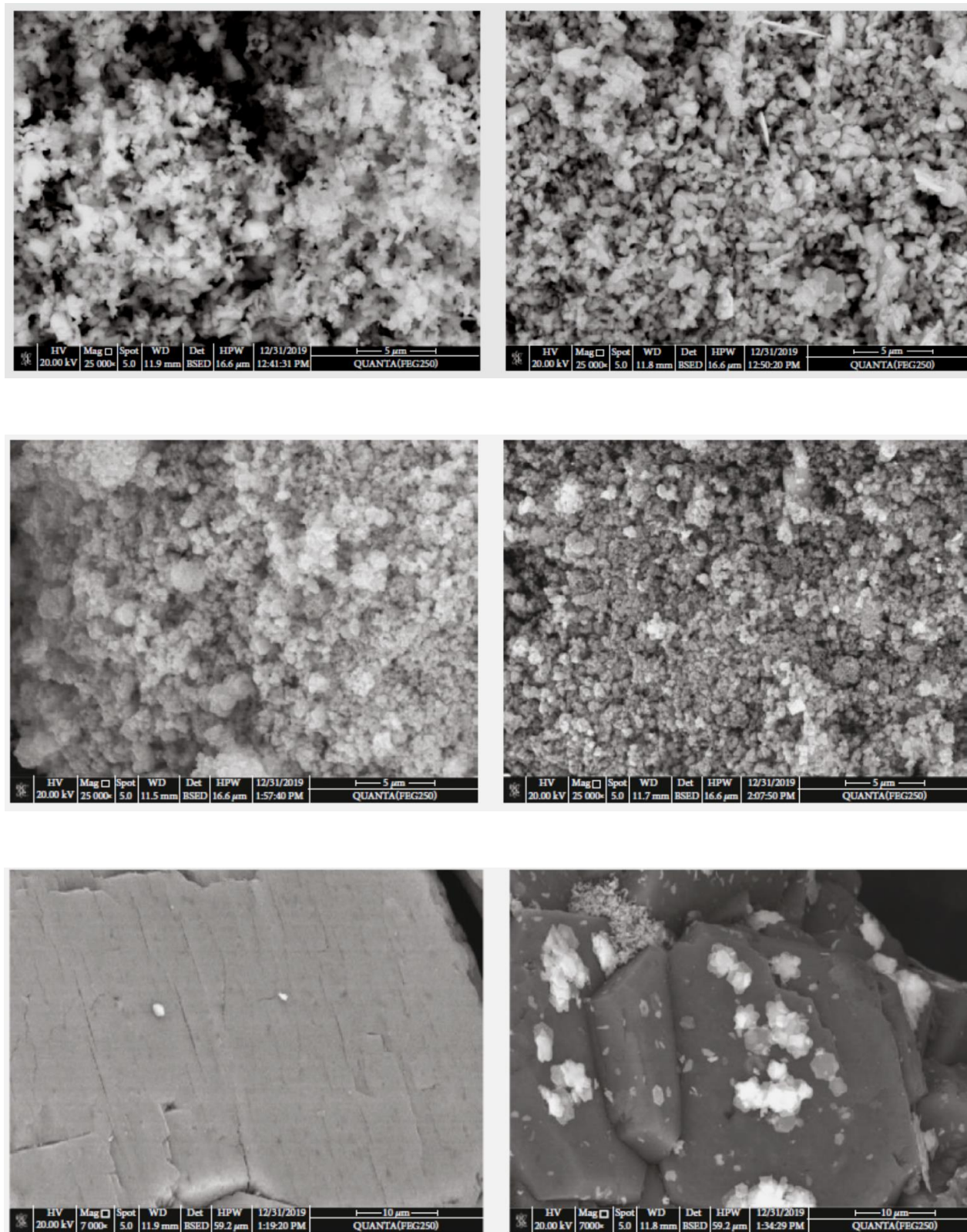
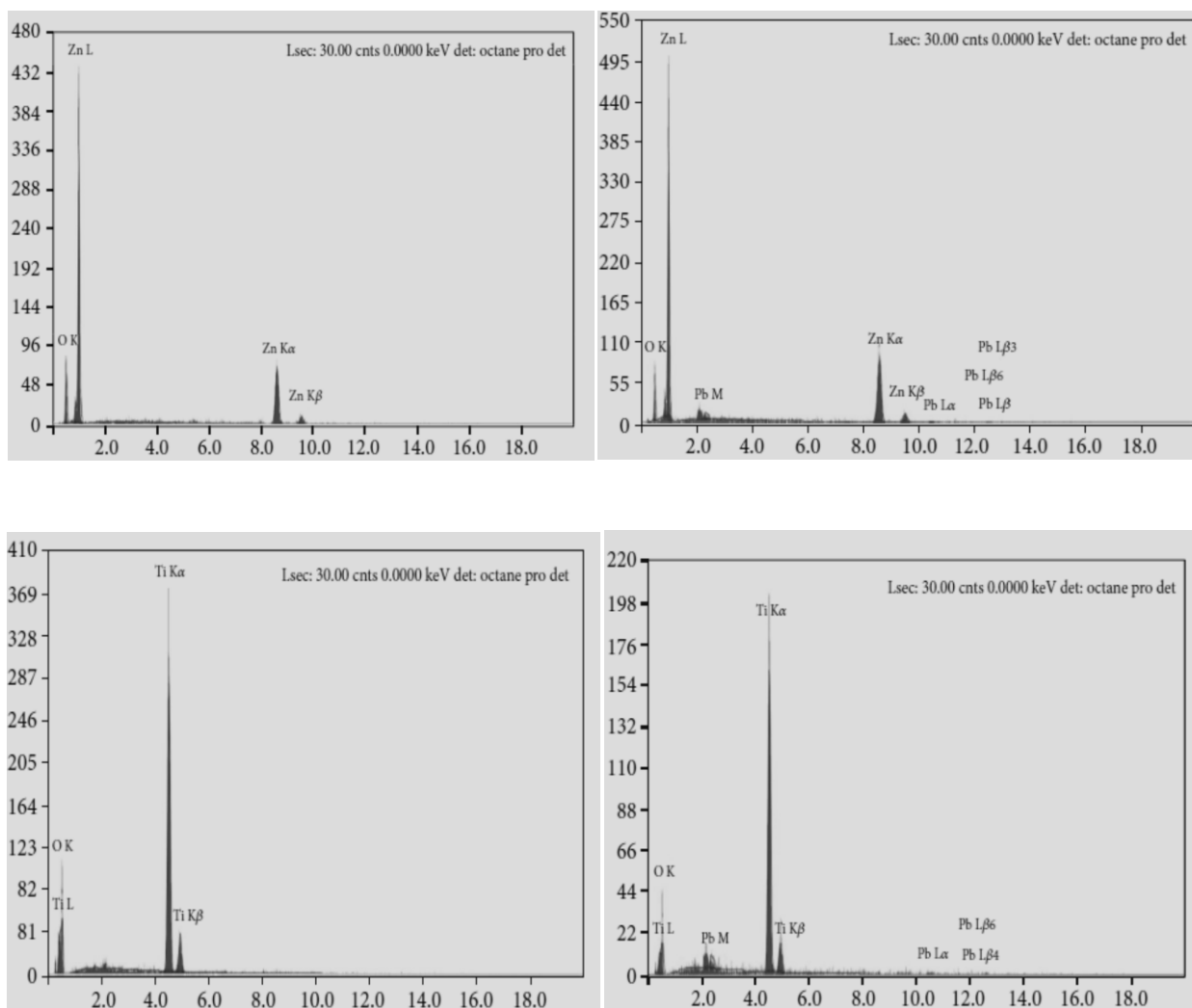


Fig 1: SEM images (a) ZnO adsorbent with no adsorption (b) ZnO adsorbent with Pb²⁺ion adsorption (c) TiO₂ adsorbents with no adsorption (d) TiO₂ adsorbents with Pb²⁺ion adsorption (e)Al₂O₃ adsorbent with no adsorption (f) Al₂O₃ adsorbent with Pb²⁺ion adsorption.

However, elemental, chemical compositional analysis of adsorbents and trace elements amount were determined with the EDX-spectral information. Further, Pb²⁺ ion uptake onto ZnO, TiO₂ and

Al_2O_3 surface have been confirmed through EDX spectral analysis, as it was shown in fig 2(a)-2(f). In contrast, Pb^{2+} ion uptake signals were shown in fig. 2(b), 2(d) and 2(f) except fig. 2(a), 2(c) and 2(e) wherein; only Zn^{2+} , Ti^{2+} and Al^{3+} signals were prominently displayed. This fascinating experiment affirms the uptake of Pb^{2+} ion onto the surface of ZnO , TiO_2 and Al_2O_3 adsorbents. Shown figures 2(a), 2(c) and 2(e) represent no characteristic signals for any metal ions except Zn^{2+} , Ti^{2+} and Al^{3+} , respectively. On the other hand, Pb^{2+} ion signals were observed in figures 2(b), 2(d) and 2(f).



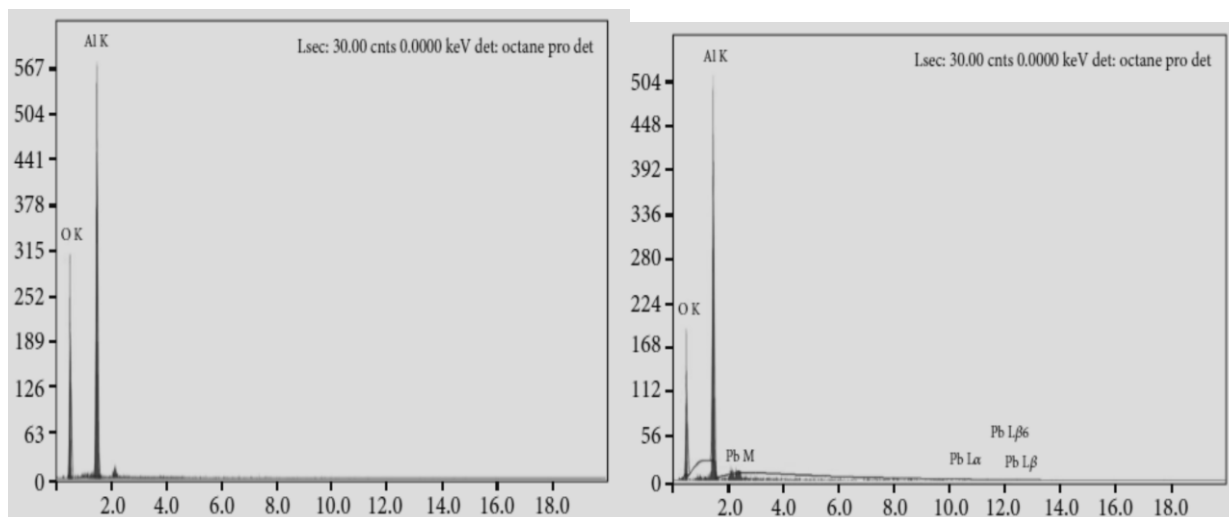


Fig (2a-2f)EDX spectral pattern analysis

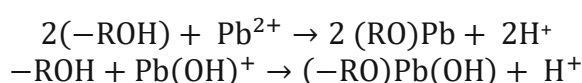
Fig 2(a) unpacked ZnO space 2(b) packed ZnO space 2(c) unpacked TiO₂ space 2(d) packed TiO₂ space 2 (e) unpacked Al₂O₃ space 2 (f) packed Al₂O₃ space.

3.2 Adsorbent surface phenomenon assessment

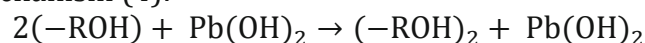
3.2.1 Solution pH Influence

An influence of a four different pH, namely, 3, 5, 7 and 9 on the percentage of Pb²⁺ ion removal was examined by means of adsorption phenomenon. While investigating pH influence on adsorption phenomenon, the adsorbent mass of 0.02g with 25 ml of contaminated water is kept constant. Initially, 100ppm Pb²⁺ion concentration was kept at room temperature (29 ± 1°C). The prepared solution mixture was shaken at a constant 150 rpm for 120 min. The resultant Pb²⁺ ion and the adsorption percentage calibration were measured, and follow Equation (1). An observed adsorption process demonstrate an optimal removal efficiencies in descending order; arranged as 94.66%, 87.97% and 65.34% for ZnO, TiO₂ and Al₂O₃respectively, at a particular pH 7.0(fig 4a). An adsorption percentage increment was observed as the solution pH will increased to pH 3.0 to 7.0. Although, the percentage increment in adsorption is account of negatively charged prominence on to adsorbent surface, as the solution pH increased subsequently, this phenomenal event is actually dependent on electrostatic force of attraction over repulsive force. Hence more interaction of Pb²⁺ ion with their adsorbents functional groups could take place or it might be happen on account of hydrogen bonding effect as it was noticed by Herrera et al. (2020) who reported to follow up the concern reaction mechanism based on the metal ion-adsorbent exchange[15].

Metal ion-adsorbent exchange reaction (3):



Hydrogen bonding mechanism (4):



However, at above pH 7.0 the percentage of adsorption phenomenon especially in case of ZnO and TiO₂ can decrease, as this marked decrement in adsorption phenomenon is carried out until and unless solution pH approach to 9.0 on account of hydroxyl complexes formation. Similarly (fig.3) shows the increment in Al₂O₃ adsorption percentage despite their pH value is reached to the 9.0 point of charge.

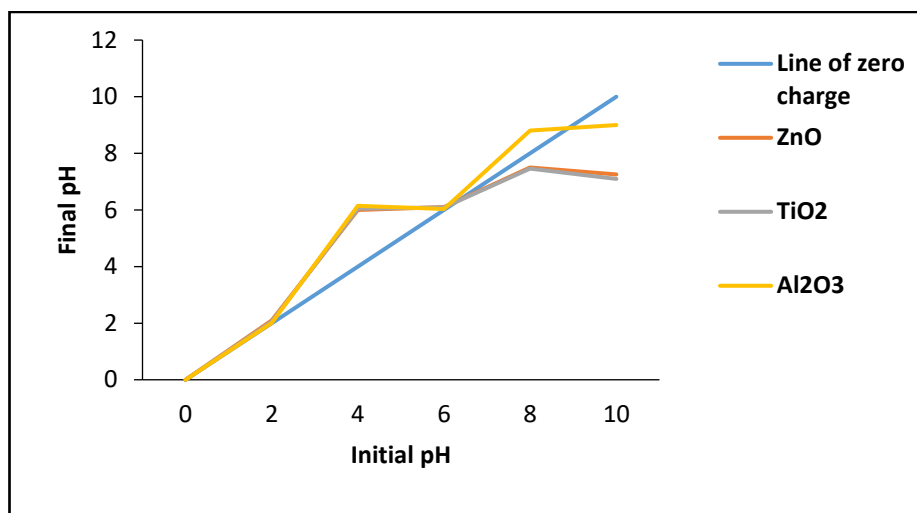


Fig.3pH drift method for all three adsorbents

From this experiment, it was concluded that greater adsorption behavior of Pb²⁺ ions could occur when there is a lesser positive charged ion present onto adsorbent surface. Therefore; the maximal adsorption of Pb²⁺ ion was observed to be take place at optimum pH=7.0. Underneath this optimal value, a lesser chance of interaction between the lead (Pb²⁺) and hydronium ions might be a good reason for reduction in adsorption efficiency compared to higher pH. Beyond pH=7.0 precipitation reaction is promoted but do not allow adsorption process to be persistent in a significant way.

3.2.2. Adsorbent doses effect

This experimental procedure was conducted at 0.01, 0.02, 0.03, 0.04 and 0.05 g adsorbents doses per 25ml of the contaminated aqueous solution at the optimal pH value. Initially Pb²⁺ ions concentration is kept 100 ppm at 29±1°C with constantly requirement of shaking at 150 rpm for 120mins. The final Pb²⁺ ion concentration and the adsorption percentage were measured with the help of Eq. (1). The study results revealed that the maximal removal efficacies were 95.27%, 90.46%, and 70.8% for ZnO, TiO₂, and Al₂O₃ respectively, at a corresponding adsorbent dosage of 0.05g, their relevant results were shown in Fig 4(b). Shown fig 4(b) reflect the consistent increment in adsorbent dosage from 0.01 to 0.05 g provokes the adsorption percentage and it may be attributed due to more availability of active binding sites for a better adsorption phenomenon. Thus, it confirms that Pb²⁺ ions are specific to the adsorbent active binding sites at optimal (0.05g)

adsorbent dosage and it would be a perfect optimal dosage of adsorbents for further experimental studies.

3.2.3. Effect of Contact Time

The perfect contact time establishes a good interaction between the adsorbent and Pb^{2+} ions, it is one of the important factor to determine the suitable adsorbent. This parameter actually examined the impact of different contact time i.e. 15, 30, 60, 90, and 120 mins on the adsorbent and Pb^{2+} ions interactions at optimal pH value (7.0) with adsorbent dose 0.05g per 25ml of contaminated solution respectively, at room temperature of $29 \pm 1^\circ C$. On the other hand, Pb^{2+} ion removal percentage increases sharply at 120 mins and it was observed that the 96.17% of maximal removal efficacy was encountered in ZnO compared to TiO_2 , and Al_2O_3 respectively, as illustrated in Fig 4(c). This set of experiment revealed that the adsorption process consistently show increment as the contact time increases from 15 to 120 mins for all undertaken adsorbents. In addition, Pb^{2+} ion removal was found to be enhanced drastically within the first 15 mins on account of sufficient number of available active binding sites onto the adsorbent surface. Subsequently within 90 mins equilibrium is achieved when all the available sites of adsorbent are almost saturated and no significant surface change was noted on lead uptake by adsorbents until 120 mins.

3.2.4. Effect of initial concentration of lead ions

The influence of initial concentration of lead ions on adsorption percentage of adsorbents was examined in this section. For this purpose, different initial concentrations of Pb^{2+} ion, such as 50, 75, 100, 125, and 150 ppm were undertaken at the optimal pH and adsorbent dosage state. An obtained result from previous batches was studied under the defined experimental conditions.

Fig.4(d) showed the significant level of Pb^{2+} ion removal (around 96.17%) by ZnO adsorbent was achieved at 100 ppm initial concentration followed by TiO_2 (91.75%) and least observed in Al_2O_3 (79.50%) respectively. These observations indicate the lead ions percentage uptake by adsorbents increases when the initial concentration of lead ions increases to a certain extent. The exact percentage of increment of adsorption for all three adsorbents was observed in high to low order since maximum adsorption for ZnO from 93.55% to 96.17%, followed by TiO_2 from 85.88 to 91.75% and then for Al_2O_3 from 61.50 to 79.50%. This percentage increment in adsorption was found to be enhanced when the initial concentration of Pb^{2+} ion is increased from 50 to 150 ppm. Later on, the percentage of Pb^{2+} ion removal decreases as the initial Pb^{2+} ion concentration increases to maximal 150 ppm concentration. This could be due to the high availability of binding sites at adsorbent surface for Pb^{2+} ion at initial stage of adsorption compared to later stages of adsorption. Therefore, adsorption process delayed the Pb^{2+} ion removal from industrial waste water streams[16-17].

3.2.3 Effect of Temperature

This set of experiment highlight the influence of solution temperature on Pb^{2+} ion removal *via* adsorbents use. Exploration of Pb^{2+} ion adsorption was conducted at 20°C, 30°C and 40°C under an optimal pH 7.0, adsorbents dose (0.05g) and 25 ml quantity of 100 ppm initial Pb^{2+} ion concentration. The obtained result show the adsorption percentage increment as the solution temperature steadily increased from 20°C to 40°C. In this context, all selected adsorbents had maximal Pb^{2+} ion adsorption efficacy at 40°C and shows the (98.43%) maximal adsorption efficacy for ZnO followed by TiO_2 (96.45%) and least (85.50%) observed in Al_2O_3 , respectively as shown in fig 4(e). However, the exact percentage increment in adsorption for all three adsorbents was observed in ZnO from 93.55% to 96.17%, followed by TiO_2 from 85.88 to 91.75% and least one in Al_2O_3 from 61.50 to 79.50% as the temperature increases. The shown results indicate that governing adsorption process for Pb^{2+} ion uptake is actually worked in an endothermic manner for all respective adsorbents.

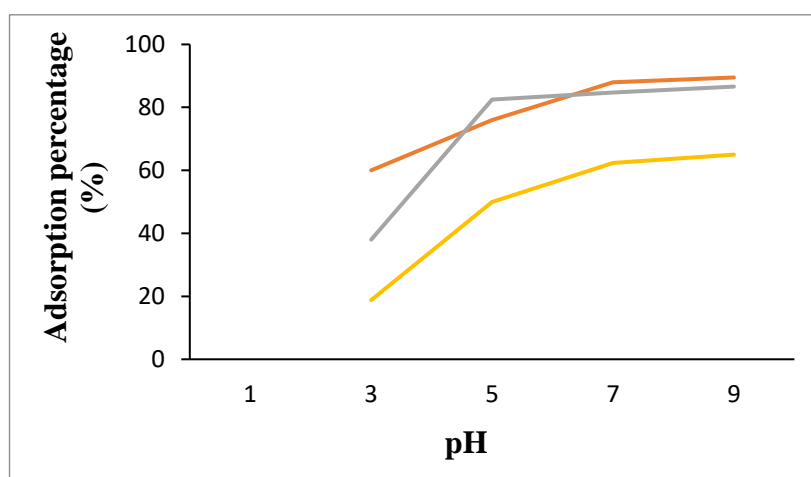


Fig 4(a) Effect of Initial pH values

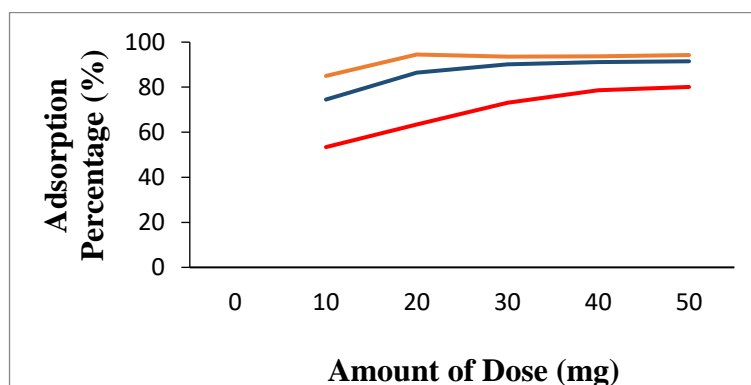


Fig 4 (b) Effect of Adsorbent dosage (mg)

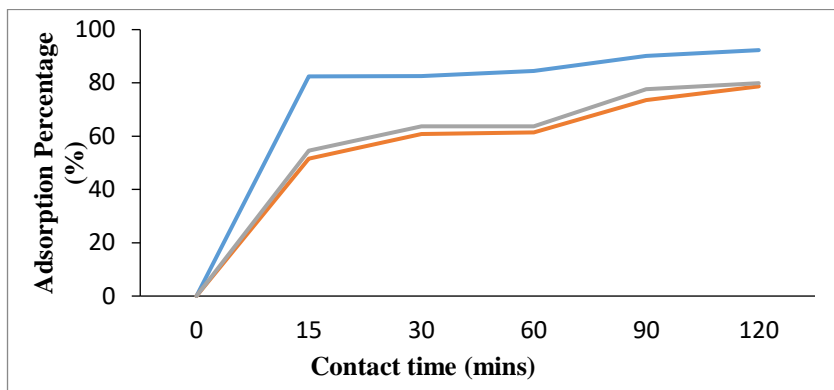


Fig 4 (c) Effect of Contact time (mins)

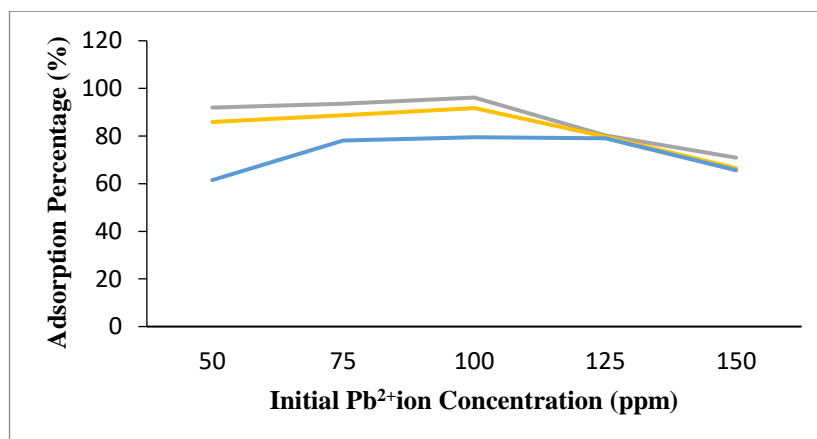


Fig 4 (d) Effect of Initial Pb²⁺ ion concentration (ppm)

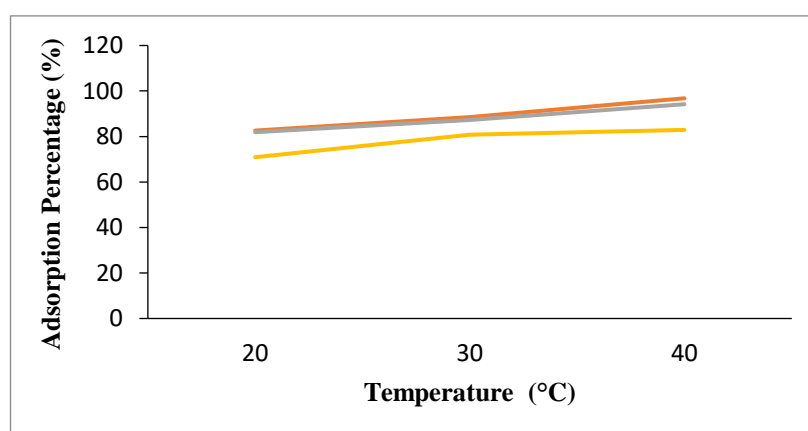


Fig4 (e) Effect of Temperature (°C)

Fig.4(a-e) Influence of different physiochemical parameters on Pb²⁺ ion adsorption onto ZnO surface (upper line graph), TiO₂ surface (Middle line graph) and Al₂O₃ (Lower line graph) surface under optimized (a) Initial pH (b) adsorbent dosage (mg) (c) contact time (mins) (d) initial Pb²⁺ ion concentration (ppm) and (e) temperature (°C) conditions.

3.3 Evaluation of Adsorption behavior

The lead ion adsorption rate onto adsorbent surface was calibrated as per adsorption kinetic models. Consequently, the three kinetic models, namely, pseudo-first order, pseudo-second order and Elovich equation were tested to measure accurately the Pb²⁺ ions adsorption rate *via* using the

results relevant to lead adsorption at different contact time. The Pseudo first order model, Pseudo-second order model, and Elovich model were expressed *via* using the (5), (6) and (7) respective, equations. The following equations were given below to accurately calibrate Pb^{2+} ions uptake rate by adsorbents in a reproducible manner (Tran, 2017; Sani, 2016).

$$\text{Log} (Q_{eq} - Q_t) = \log Q_{eq} - \frac{K_1}{2.303} t \quad \text{EQ. (5)}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_{eq}^2} + \frac{1}{Q_{eq}} t \quad \text{EQ. (6)}$$

$$Q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \quad \text{EQ. (7)}$$

Whereas; Q_{eq} is the mass of absorbed pollutant per unit weight of adsorbent at equilibrium (mg/g), Q_t is the adsorbed amount of adsorbent at time (t)(mg/g), K_1 is the pseudo-first order equation constant(min^{-1}), t is time (min), K_2 is the rate constant of pseudo-second order equation($\text{g}/\text{mg}\cdot\text{min}$), a is an initial rate of adsorption (mg/g.min) and $1/b$ is a parameter relative to the number of adsorption sites on the surface of the adsorbents(mg/g).

The Pseudo-second order kinetic model is a preferred model and it shows the significant correlation coefficient (r^2) outcome. The Pseudo-second order was found to be greater (r^2) value compared to the pseudo-first order model and Elovich equation, which concluded that the pseudo-second order model consider as suitable kinetic model in describing the adsorption process. These illustrated results in table 1 were in support of chemisorption and it is associated with rate-limiting reaction.

Table.1 Kinetic models and parameters for Pb^{2+} ion removal on different adsorbents surface.

Kinetic models	Kinetics parameters		ZnO	TiO ₂	Al ₂ O ₃
Elovich equation	a	mg/g.min	9.35×10^6	1.03×10^{12}	1.95×10^3
	b	g/mg	0.431	0.71	0.32
	r^2		0.701	0.94	0.84
Pseudo first order	K_1	min^{-1}	8.25×10^{-3}	2.17×10^{-2}	5.6×10^{-2}
	Q_{eq}	mg/g	6.78	3.40	15.52
	r^2		0.86	0.85	0.89
Pseudo second order	K_1	min^{-1}	9.30×10^{-4}	1.8×10^{-3}	7.3×10^{-3}
	Q_{eq}	mg/g	48.6	45.3	34.89
	r^2		0.99	0.999	0.99

4. Conclusion

This research work comprehensively investigated the removal of lead ions by means of metal oxides based adsorbents, namely, zinc oxide (ZnO), titanium dioxide (TiO₂) and aluminium oxide (Al₂O₃). In addition, affect of different physiochemical parameters such as solution pH, adsorbent dosage, contact time, initial concentrations and temperature on the adsorbents, adsorption behavior and removal efficiency for Lead (Pb^{2+}) ion from industrial waste water was investigated. More

elaborately; ZnO exhibit good adsorption capacity for Pb^{2+} ion, which would be confirmed significantly through the pseudo-second order kinetics when compared to titanium dioxide (TiO_2) and aluminium oxide (Al_2O_3). As per chemical and morphological basis, it was concluded that lead ion removal from polluted water is seem to be higher in ZnO followed by TiO_2 and least one observed in Al_2O_3 . The major advantage of this research work is to recover toxic lead ion in a significant amount from contaminated water streams with the use of zinc oxide as adsorbent. Although, this study confirms that ZnO had greater capacity to remove heavy metal ions and to achieve considerable contribution in environmental remediation especially to purify contaminated water stream bodies.

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