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REMOVAL OF METALS FROM MINING WASTEWATER BY USING NANO ABSORBENTS

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²Professor, Department of Civil Engneering, Basaveshwar Engineering College, Bagalkot -587102, India. comparison to the overall mass of the Earth. [1]

ABSTRACT

Considering the current water scarcity and environmental issues linked with waste water, research into current treatment technologies is critical. Metals, being a highly poisonous substance with suffocating properties, are regarded as one of the environmental pollutants in a wide spectrum of industrial effluents. The current work sought to investigate metal absorption utilizing TiO₂ and ZnO nano absorbent. Two sets of tests are planned to assess metal absorption performance. Metals are absorbed by TiO₂ in the first experimental setup and ZnO in the second. These experiments take place in a batch reactor. The metal removal effectiveness of TiO₂ and ZnO is investigated in batch studies utilizing the Response Surface Methodology (RSM).

In this study the maximum % reduction of iron is 50.41% at pH 6, contact time 30 min and dosage is 0.04 gm of ZnO nano absorbent. Similarly for chromium it is 36.56 % reduction occurred at pH 6 and contact time 90 min and dosage of 0.08 gm of ZnO absorbent. The ZnO Absorption is effective for metal reduction in batch absorption process

Keywords: metal reduction, nano-absorbents, mining wastewater

INTRODUCTION

As we know freshwater is necessary for both to human being and wildlife. The availability of potable water is essential for living a healthy existence. Around 1.386 billion cubic kilometres of water are present on earth. About 97 percent of it is made up of salt-watercontaining seas and oceans. A little more than 1% is distributed as rivers, lakes, ground water, and water vapour, whereas more than 2% is made up of ice caps and glaciers. Almost 97 % of the water in the hydrosphere exists as seas and oceans. These are all salty bodies of water. They are not ideal for direct consumption such as drinking or cooking, nor for use in industries or irrigation. [1]

Fresh water accounts for only 3% of all accessible water on the planet. Looking only at the further dispersion of freshwater, we can see that nearly 66.7% majority is frozen up in the form of ice caps and glaciers. Groundwater accounts up approximately 30.1% of the total. Only 0.3% of surface water is directly available on the ground surface; the remaining 0.9 % exists as water vapour and soil water. Lakes, wetlands, and rushing water like rivers share 0.3% of the available surface water. A very small concentration of this occurs as biological water. If some of the water on Earth were formed into a sphere, the diameter of that water ball would be approximately 1385 km. In terms of volume, it would be a very little ball in

It is generally recognized that aquatic environments are directly or indirectly the final destinations of these compounds, and managing heavy metal-containing wastewater has been one of the most important concerns in recent decades in order to preserve environmental quality. The increased usage of a wide range of

metals in many industries, as well as the habit of releasing untreated waste into water bodies, has resulted in an increase in HMs in water resources. [2]

Metals

Metals are metallic elements with a comparatively high density in comparison to water. Based on the assumption that heaviness and toxicity are linked, heavy metals also include metalloids that can cause toxicity at low levels of exposure. Heavy metals are elements with atomic weights ranging from 63.5 to 200.6 and specific gravities greater than 5.0. [3] Nevertheless, human exposure has increased considerably due to an exponential expansion in their use in a variety of industrial, agricultural, residential, and technology applications. Heavy metals are naturally occurring elements found throughout the earth's crust; however, the majority of environmental contamination and human exposure are caused by anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds. [3]

Heavy metals and metals are harmful because they tend to accumulate in the body. Bioaccumulation is defined as an increase in the concentration of a chemical in a biological organism over time in comparison to the concentration of the chemical in the environment. When compounds are taken up and stored quicker than they are broken down (metabolized) or expelled, they accumulate in living things. Heavy metals can enter a water supply from industrial and consumer waste, as well as acidic rain, which break down soils and releases heavy metals into streams, lakes, rivers, and groundwater. [2, 3]

Because of our growing use of these substances, metals are now plentiful in our drinking water, air, and soil. They can be found in almost every aspect of modern consumer culture, from building materials to cosmetics, pharmaceuticals to processed foods, fuel supplies to agents of destruction, appliances to personal care goods. It is extremely difficult to avoid exposure to any of the several dangerous heavy metals that are so widespread in our environment. Heavy metal emissions to the environment happen in many different of operations and mechanisms, including those to the air (e.g., during combustion, extraction, and processing), surface waters (through runoff and releases from storage and transport), and soil (and hence into groundwater's and crops) [5]

Metals are generally released during their mining and processing activities. Heavy metal contamination is prevalent in mining locations and historic mine sites, and pollution decreases with increasing distance from the mining site. These metals are leached out and moved downstream or run-off to the sea by acidic water in sloppy regions. Water bodies are severely polluted as a result of mining activity. The risk of contamination increases when metalbearing ores are mined rather than naturally exposed ore bodies through erosion, and when mined ores are placed on earth surfaces in hand dressing procedures. Metals are carried via rivers and streams as dissolved species in water or as part of suspended sediments (dissolve species in water have the greatest potential of causing the most deleterious effects). They may then be held in river bed sedimentary seeps into underground water, contaminating water from underground sources, particularly wells, with the level of pollution dependent on the well's proximity to the mining site. [4]

Table 1 Drinking water standards as per BIS- 10500-2012

Tuble 1 Brinking water standards as per Bis 10000 2012							
Metal	Acceptable Limit (mg/L)	Permissible Limit					
Lead	0.01	No relaxation					
Copper	0.05	1.5					
Chromium	0.05	No relaxation					
Cadmium	0.003	No relaxation					
Iron	0.3	No relaxation					
Cyanide	0.05	No relaxation					
Mercury	0.001	No relaxation					
Nickel	0.02	No relaxation					
arsenic	0.01	0.05					

II. ISSUES AND CHALLENGES

Although a few heavy metals have bio-importance as trace elements, the bio toxicity of several of them in human biochemistry is of critical challenge. As a result, a thorough understanding of the variables that cause bio toxicity, such as concentrations and oxidation states, is required. It is also critical to understand their origins, leaching pathways, chemical transformations, and modes of deposition in order to harm the environment, which fundamentally sustains life. Metals enter the environment from both natural and manmade sources.

They leach into subsurface waters, where they move along water routes and finally deposit in the aquifer, or they are swept away by run-off into surface waterways, resulting in water and soil contamination. Animal poisoning and toxicity are usually caused by exchange and coordination mechanisms. By this way the metals are harm to the human health as the bioaccumulation and bio magnification takes place.

OBJECTIVES

- To collect and analyses of the heavy metals contaminated effluent from mining area.
- To study the Absorption efficiency of zinc and titanium Nano metal oxides in removal of metals (Iron, copper and chromium), from effluent from mining area.
- To study how variables like adsorbent dose, pH, and contact duration affect the final result absorption.

IV. **MATERIAL**

Instruments

- Digital pH meter
- Agitator
- weighing machine
- Spectrophotometer

Chemicals

- Titanium dioxide Nano material
- Zinc oxide Nano material
- Hydrochloric acid (HCL) (0.1N)
- Sodium hydroxide (NaOH) (0.1N)
- Nitric acid (HNO₃)
- Hydroxyl amine solution
- Ammonium acetate buffer
- Phenanthroline solution
- 1-5 Diphenylcarbazide
- Acetone
- Ammonium hydroxide

Sample Collection:

Waste water samples were taken from the mining region. Samples were collected in good quality screw-capped high density pre sterilized polypropylene bottles, each with a 1lt capacity, correctly labelled, and examined for trace metals in a laboratory.



Fig. 1 Sample collection and storage

Qualitative Analysis of Sample

The characterization study (Table 3) was carried out right away in the lab

Table 2 Characteristics of Mining wastewater

Characteristics	Value
Iron concentration	4.5 mg/l
Chromium concentration	0.68 mg/l
Copper concentration	0.32 mg/l
рН	6.5

Experimental Set Up

Iron content detection (Phenanthroline method): First we Take 0, 1, 2, 3, 4, 5 mL standard Iron solution in a clean Nessler tube and distilled water up to 50 mL mark exactly in all Nessler tubes. This results in standard Iron concentrations of 0 mg/l, 0.2 mg/l, 0.4 mg/l, 0.6 mg/l, 0.8 mg/l, and 1.0 mg/l. In a beaker, place 50 ml of wellshaken sample (The solution whose iron content is to be measured). Then, add 2 mL of concentrated HCl, immediately followed by 1 mL of hydroxylamine solution to the previously prepared sample. Boil until the volume is decreased to 15 to 20 ml. Allow it cool to room temperature before transferring to a Nessler tube. Add a few glass beads and bring to a boil to ensure that all of the iron is dissolved. 10 mL ammonium acetate buffer and 4 mL phenanthroline solution are added, then dilute with distilled water to make a mark, Allow at least 10 to 15 minutes for maximum colour development after thoroughly mixing. Compare the sample's colour to set standards to determine the iron concentration in mg/l.



Fig 2: Standard Iron solution concentration

Chromium content detection (DPC method)

The diphenylcarbazide assay for measuring Cr was derived from traditional processes for examining mining waste water contaminated with chromium. 10ml of distilled water was added, followed by 1 ml of Diphenylcarbazide solution (0.25 percent w/v) in acetone, then add known standard chromium of various concentrations, and finally 1 to 2 drops of HnO₃ solution. At 540nm, absorbance measurements of standards of 0, 0.2, 0.4, 0.6, 0.8, and 1 mg/L were recorded in a spectrophotometer. Later computations were performed to calculate the chromium content. And graphs for optical density (OD) v/s concentration were created.

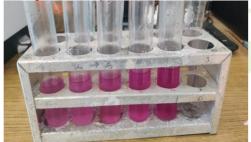


Fig 3: Standard Chromium solution

Table 3: Calibration values of chromium

Concentration	Absorbance
0	0.0
0.2	0.948
0.4	1.0302
0.6	1.1402
0.8	1.162
1.00	1.1946

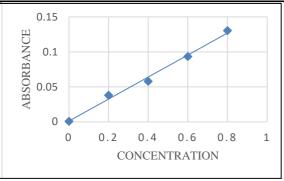


Fig 4: Calibration curve of chromium

Batch absorption study

The examination of the absorption process on iron, chromium, and copper removal was focused on three scenarios. The following factors are taken into consideration in these cases: adsorbent dose, pH, and agitation contact time. To execute the standard experiment, the maximum and lowest values of pH, adsorbent dose, and contact time are entered into DESIGN EXPERT 11. Then by conducting experiments to identify the optimal pH, adsorbent dosage, and contact time. Then removal efficiency is calculated by below formula

Removal efficiency= $((C_0-C_i)/C_0)*100$

Where:

C_o is the initial concentration of heavy metal

C_i is final concentration



Fig 5: Agitation of sample

Optimization employing Box Behnken design

Box Behnken statistical design is an effective way for quickly optimizing a system. Using Design Expert Software, the BoxBehnken design (BBD) was applied to optimize Tio₂ and Zno nanoparticles. At low and high levels, Tio₂ and Zno concentrations (factor A), pH (factor B), and contact time (factor C) were chosen as independent variables. To adapt the replies to the proper mathematical model produced by design, many statistical measures such as the probability value (p-value), the regression coefficient (R2) value), the Fisher model value (F value), and the lack of fit F value were utilized.

RESULTS AND DISCUSSION

Removal of iron by various Nano absorbents

Removal of iron by TiO2

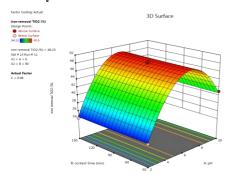


Fig 6: 3D graph expressing the interconnection of two parameters A: pH and B: contact time

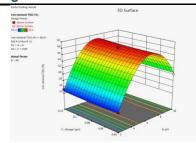


Fig 7: 3D graph expressing the interconnection of two parameters A: pH and C: dosage

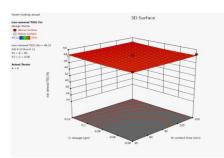


Fig 8: 3D graph expressing the interconnection of two parameters C: dosage and B: contact time

The 3D graphs are showing the reduction of iron concentration in the mining wastewater. The initial concentration of iron content where 4.5 mg/l in the raw mining wastewater. Then according to the design-expert 11 the experiments were carried out and the results were obtained. The minimum percentage of reduction when TiO₂ is added to the wastewater is 34.12 % where the pH is 2, contact time is 150 min, and the dosage of TiO2 is 0.08 gm. Similarly the maximum percentage of reduction when TiO₂ is added to the wastewater is 48.6 % where the pH is 6, contact time is 150 min, and the dosage of TiO₂ is 0.04 gm.

Absorption of iron using TiO2

Table 4: Absorption process design matrix final concentration and movel percented

removal percentage									
Run	A:pH	B:contect time(min)	C:dosage (gm)	Iron removal TiO2 (%)					
11	6	90	0.08	48.23					
1	6	90	0.08	48.23					
12	6	90	0.08	48.2					
4	6	30	0.12	48.12					
5	6	30	0.04	48.2					
2	6	150	0.04	48.6					
13	6	150	0.12	48.45					
14	6	90	0.08	47.9					
17	6	90	0.08	47.89					
10	10	90	0.04	40.12					
15	10	30	0.08	41.02					
6	10	90	0.12	41.25					
3	10	150	0.08	41.21					
8	2	90	0.12	35.23					
9	2	90	0.04	34.52					
7	2	150	0.08	34.12					
16	2	30	0.08	34.26					

Fit Summary

Table 5: Iron removal TiO₂

ANOVA for Quadratic model

Table 6: Iron removal TiO2

Table 0: Iron removal 1102										
Source	Sum of Squares	df	Mean Square	F-value	p- value					
Model	547.43	9	60.83	317.17	< 0.0001	significant				
A-pH	81.09	1	81.09	422.84	< 0.0001					
B- contect time	0.0761	1	0.0761	0.3966	0.5489					
C-dosage	0.3240	1	0.3240	1.69	0.2348					
AB	0.0272	1	0.0272	0.1420	0.7175					
AC	0.0441	1	0.0441	0.2300	0.6462					
ВС	0.0012	1	0.0012	0.0064	0.9385					
A ²	464.21	1	464.21	2420.60	< 0.0001					
B ²	0.0164	1	0.0164	0.0858	0.7781					
C ²	0.1520	1	0.1520	0.7926	0.4029					
Residual	1.34	7	0.1918							
Lack of Fit	1.22	3	0.4050	12.72	0.0163	significant				
Pure Error	0.1274	4	0.0318							
Cor Total	548.77	16								

The Model F-value of 317.17 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

 Table 7: Fit Statistics

Std. Dev.	0.4379	\mathbb{R}^2	0.9976
Mean	43.27	Adjusted R ²	0.9944
C.V. %	1.01	Predicted R ²	0.9642
		Adeq Precision	42.1889

The **Predicted R**² of 0.9642 is in reasonable agreement with the **Adjusted R** 2 of 0.9944; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 42.189 indicates an adequate signal. This model can be used to navigate the design space.

Source	Sequential p-value	Lack of Fit p- value	Adjusted R ²	Predicted R ²	
Linear	0.5386	< 0.0001	-0.0480	-0.5779	
2FI	1.0000	< 0.0001	-0.3622	-2.5238	
Quadratic	< 0.0001	0.0163	0.9944	0.9642	Suggested
Cubic	0.0163		0.9991		Aliased

Removal of iron by ZnO

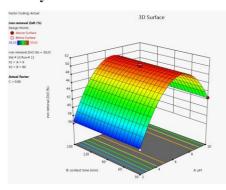


Fig 9: 3D graph expressing the interconnection of two parameters

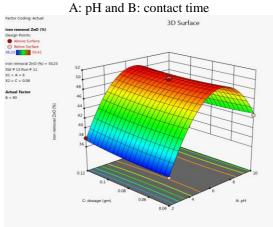


Fig 10: 3D graph expressing the interconnection of two parameters

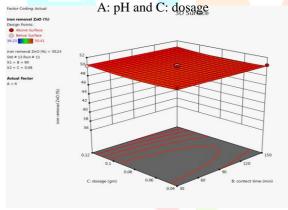


Fig 11: 3D graph expressing the interconnection of two parameters C: dosage and B: contact time

The 3D graphs are showing the reduction of iron concentration in the mining wastewater. The initial concentration of iron content where 4.5 mg/l in the raw mining wastewater. Then according to the design-expert 11 the experiments were carried out and the results were obtained. The minimum percentage of reduction when ZnO is added to the wastewater is 36.23 % where the pH is 2, contact time is 90 min, and the dosage of ZnO is 0.04 gm. Similarly the maximum percentage of reduction when ZnO is added to the wastewater is 50.41 % where the pH is 6, contact time is 30 min, and the dosage of ZnO is 0.04 gm. This shows that when the ZnO is added to the wastewater it is more reactive in slightly in acidic media rather than basic media.

Fit Summary of iron

Table 8: Iron removal ZnO

Source	Sequential p-value	Lack of Fit p-value	Adjuste d R ²	Predict ed R ²	
Linear	0.5522	< 0.0001	-0.0533	-0.5913	
2FI	0.9997	< 0.0001	-0.3679	-2.5604	
Quadratic	< 0.0001	0.2115	0.9942	0.9727	Sugg ested
Cubic	0.2115		0.9964		Alias ed

ANOVA for Quadratic model

Table 9: Iron removal ZnO

Source	Sum of Square s	df	Mean Squar e	F- value	p- value	
Model	523.40	9	58.16	306.48	< 0.000 1	significa nt
А-рН	75.28	1	75.28	396.70	< 0.000 1	
B- contact time	0.0595	1	0.0595	0.3136	0.592 9	
C- dosage	0.3160	1	0.3160	1.67	0.237 9	
AB	0.0676	1	0.0676	0.3562	0.569 4	
AC	0.4096	1	0.4096	2.16	0.185 2	
ВС	0.0000	1	0.0000	0.0001	0.991	
A ²	445.98	1	445.98	2350.2 7	< 0.000 1	
B ²	0.0028	1	0.0028	0.0147	0.906 9	
C ²	0.5788	1	0.5788	3.05	0.124	
Residu al	1.33	7	0.1898			
Lack of Fit	0.8502	3	0.2834	2.37	0.211	not significa nt
Pure Error	0.4781	4	0.1195			
Cor Total	524.73	1 6				

The **Model F-value** of 306.48 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table 10: Fit Statistics							
Std. Dev.	0.4356		\mathbb{R}^2	0.9975			
Mean	45.26		Adjusted R ²	0.9942			
C.V. %	0.9625		Predicted R ²	0.9727			
			Adeq Precision	42.4614			

The **Predicted R**² of 0.9727 is in reasonable agreement with the **Adjusted R²** of 0.9942; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 42.461 indicates an adequate signal. This model can be used to navigate the design space.

Removal of chromium by various Nano absorbents

Removal of chromium by TiO2

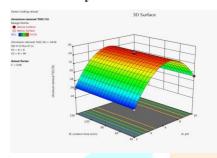


Fig 12: 3D graph expressing the interconnection of two parameters

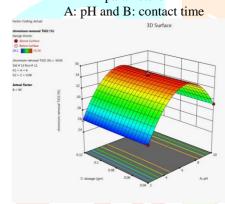


Fig 13: 3D graph expressing the interconnection of two parameters

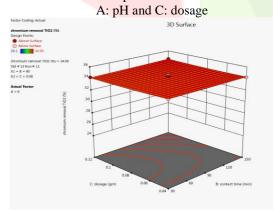


Fig 14: 3D graph expressing the interconnection of two parameters C: dosage and B: contact time

The 3D graphs are showing the reduction of chromium concentration in the mining wastewater. The initial concentration of chromium content where 0.68 mg/l in the raw mining wastewater. Then according to the design-expert 11 the experiments were carried out and the results were obtained. The minimum percentage of reduction when TiO2 is added to the wastewater is 26.1 % where the pH is 2, contact time is 30 min, and the dosage of TiO₂ is 0.08 gm. Similarly the maximum percentage of reduction when TiO₂ is added to the wastewater is 34.56 % where

the pH is 6, contact time is 90 min, and the dosage of TiO2 is 0.08 gm. This shows that when the TiO2 is added to the wastewater it is more reactive in slightly in acidic media rather than basic media.

Fit Summary chromium

Table 11: Chromium removal TiO₂

Source	Sequenti al p- value	Lack of Fit p- value	Adjuste d R ²	Predict ed R ²	
Linear	0.7420	0.000	-0.1221	-0.6832	
2FI	1.0000	< 0.000 1	-0.4584	-2.7466	
Quadrat ic	< 0.0001	0.951 9	0.9928	0.9917	Suggest ed
Cubic	0.9519		0.9883		Aliased

ANOVA for Quadratic model

Table 12: Chromium removal TiO₂

	Table 12: Chromium Temovar 1102									
Source	Sum of Squares	df	Mean Square	F-value	p- value					
Model	194.26	9	21.58	245.33	< 0.0001	significant				
A-pH	17.14	1	17.14	194.82	< 0.0001					
B- contect time	0.0630	1	0.0630	0.7162	0.4254					
C- dosage	0.0012	1	0.0012	0.0142	0.9085					
AB	0.0072	1	0.0072	0.0821	0.7827					
AC	0.0144	1	0.0144	0.1637	0.6979					
BC	0.0196	1	0.0196	0.2228	0.6513					
A ²	176.24	1	176.24	2003.23	< 0.0001					
B ²	0.0010	1	0.0010	0.0111	0.9189					
C ²	0.0288	11	0.0288	0.3277	0.5849					
Residual	0.6159	7	0.0880							
Lack of Fit	0.0456	3	0.0152	0.1066	0.9519	not significant				
Pure Error	0.5703	4	0.1426							
Cor Total	194.87	16								

The **Model F-value** of 245.33 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table 13: Fit Statistics

Std. Dev.	0.2966	R ²	0.9968
Mean	31.22	Adjusted R ²	0.9928
C.V. %	0.9500	Predicted R ²	0.9917
		Adeq Precision	36.5673

The **Predicted R**² of 0.9917 is in reasonable agreement with the **Adjusted R²** of 0.9928; i.e. the difference is less than 0.2. **Adeq Precision** measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 36.567 indicates an adequate signal. This model can be used to navigate the design space.

Removal of chromium by ZnO

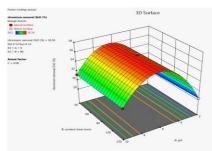


Fig 15: 3D graph expressing the interconnection of two parameters

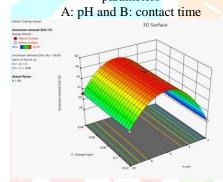


Fig 16: 3D graph expressing the interconnection of two

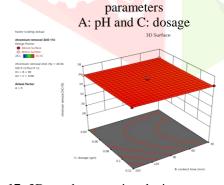


Fig 17: 3D graph expressing the interconnection of two parameters

C: dosage and B: contact time

The 3D graphs are showing the reduction of chromium concentration in the mining wastewater. The initial concentration of chromium content where 0.68 mg/l in the raw mining wastewater. Then according to the design-expert 11 the experiments were carried out and the results were obtained. The minimum percentage of reduction when ZnO is added to the wastewater is 28.1 % where the pH is 2, contact time is 30 min, and the dosage of ZnO is 0.08 gm. Similarly the maximum percentage of reduction when ZnO is added to the wastewater is 36.56 % where the pH is 6, contact time is 90 min, and the dosage of ZnO is 0.08 gm. This shows that when the ZnO is added to the wastewater it is more reactive in slightly in acidic media rather than basic media.

Absorption of chromium using ZnO

Fit Summary

Table 14: Chromium removal ZnO

Source	Sequenti al p- value	Lack of Fit p- value	Adjuste d R ²	Predict ed R ²	
Linear	0.7420	0.000	-0.1221	-0.6832	
2FI	1.0000	< 0.000 1	-0.4584	-2.7466	
Quadrat ic	< 0.0001	0.951 9	0.9928	0.9917	Suggest ed
Cubic	0.9519		0.9883		Aliased

ANOVA for Quadratic model

Table 15: Chromium removal ZnO

Tuble 10. Chromath Temoval Zho						
Source	Sum of Squares	df	Mean Square	F-value	p- value	
Model	194.26	9	21.58	245.33	< 0.0001	significant
A-pH	17.14	1	17.14	194.82	< 0.0001	
B- contect time	0.0630	1	0.0630	0.7162	0.4254	
C- dosage	0.0012	1	0.0012	0.0142	0.9085	
AB	0.0072	_1	0.0072	0.0821	0.7827	
AC	0.0144	1	0.0144	0.1637	0.6979	
BC	0.0196	1	0.0196	0.2228	0.6513	
A ²	176.24	1	176.24	2003.23	< 0.0001	
B^2	0.0010	1	0.0010	0.0111	0.9189	
C ²	0.0288	1	0.0288	0.3277	0.5849	
Residual	0.6159	7	0.0880	Í		
Lac <mark>k of Fit</mark>	0.0456	3	0.0152	0.1066	0.9519	not significant
Pure Error	0.5703	4	0.1426			
Cor Total	194.87	16				

The **Model F-value** of 245.33 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to

P-values less than 0.0500 indicate model terms are significant. In this case A, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table 16: Fit Statistics

Std. Dev.	0.2966	\mathbb{R}^2	0.9968
Mean	33.22	Adjusted R ²	0.9928
C.V. %	0.8928	Predicted R ²	0.9917
		Adeq Precision	36.5673

The **Predicted R**² of 0.9917 is in reasonable agreement with the **Adjusted R²** of 0.9928; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 36.567 indicates an adequate signal. This model can be used to navigate the design space.

CONCLUSION

The following results were reached based on the experimental examination of iron, chromium, and copper removal via absorption using zinc oxide and titanium dioxide Nano adsorbents from mining wastewater.

The removal of iron is maximum for ZnO absorbents compare to TiO_2 absorbent. The maximum reduction is 50.41% where the pH is 6, contact time is 30 min and dosage of ZnO is 0.04 gm. The minimum reduction is 48.6% occurs at pH 6, contact time is 150 and TiO_2 dosage is 0.04 gm.

The removal of chromium is maximum for ZnO absorbents compare to TiO_2 absorbent. The maximum reduction is 36.56% where the pH is 6, contact time is 90 min and dosage of ZnO is 0.08 gm. The minimum reduction is 34.56% occurs at pH 6, contact time is 90 and TiO_2 dosage is 0.08 gm.

The removal of copper is maximum for TiO₂ absorbents compare to ZnO absorbent. The maximum reduction is 47.45% where the pH is 6, contact time is 90 min and dosage of TiO₂ is 0.08 gm. The minimum reduction is 45.45% occurs at pH 6, contact time is 90 and ZnO dosage is 0.08 gm.

Absorption increases with increasing pH of solution due to successive deprotonation of hydroxyl groups on the adsorbent and electrostatic interaction between negative sites on the adsorbent and metals. When the pH of the solution was reduced, there was competitive absorption between H⁺ ions and strongly competing heavy metals. At low pH, the Nano-binding adsorbent's sites were dominated by H⁺ ions, resulting in protonated functional groups and reduced absorption.

The average reduction occurs at pH 6, contact time is 90 min and absorbent dosage is 0.08gm. And the reduction is occurs most of them in slightly in acidic media and moderate contact time and optimum dose.

The overall maximum metal reduction occurs at iron metal and the absorbent is ZnO and the minimum metal reduction occurs at chromium metal and absorbent is TiO_2 .

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