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Adsorptive Removal of Zn(II) Heavy Metal Ion from Synthetic Waste Water Using Red Mineral Soil of Pithoragarh, Uttarakhand

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Abstract

This study investigates the adsorption of zinc (II) ions onto red mineral soil. The red mineral soil has been applied as an adsorbent for the treatment of Zinc contaminated synthetic waste water. Adsorption study was assured on the basis of adsorption parameters pH, initial metal ion concentration, dosage amount, contact time and temperature. The batch equilibrium experiment results reveal that, at optimized conditions of high pH (pH 6), high metal ion concentration, more interaction time with larger amount of adsorbent (red mineral soil) shows highest adsorption efficiency. The equilibrium data were best studied on Freundlich, isotherm model. The FTIR, SEM and AAS analysis is done for required adsorption studies.

Keywords: Waste water treatment, adsorption study, Freundlich adsorption isotherm

Introduction

The high demand and less availability of useful water, has dragged the attention towards treatment of polluted aqueous system [1, 2]. In these days threat of heavy metal water pollution has become most serious issues of aqueous ecosystem[3] and hence aqueous contamination by toxic heavy metals is a major concern to cure. For this adsorption can be an alternative method for the treatment of heavy metal polluted waste water. The treatment of heavy metal contaminated water is of special concern due to their recalcitrance and persistence in the environment [4, 5]. In contrast to organic pollutants, heavy metals are non-biodegradable and tend to bioaccumulate in living organisms. Many of these metals are recognized for their toxicity and potential carcinogenicity [6]. Toxic heavy metals of particular concern, in treatment of industrial wastewater includes chromium, cobalt, copper, cadmium, zinc, mercury, nickel, iron, lead etc. The presence of heavy metals in amount greater than what allowed in water bodies is hazardous to living beings. Zinc is an essential transition metal typically found in its divalent state. While it is important for health, excessive exposure can lead to toxicity. This can occur through inhaling industrial fumes, overusing supplements, applying denture adhesives, accidentally ingesting coins, or errors in preparing intravenous nutrition. The World Health Organization (WHO) sets a safe limit of 5.0 mg/L for zinc in drinking water to prevent health issues. Elevated zinc levels in wastewater usually result from metal production, chemical and paper industries, galvanizing, and plating. Toxicity symptoms include nausea, vomiting, stomach cramps, Anemia, reduced HDL cholesterol, fatigue, abdominal pain, copper deficiency, and weakened immune response [7-10]. So, it is very essential to remove these toxic heavy metals from the wastewater for healthy and safe environment.

The removal of heavy metals from water and soil surrounding industrial facilities has long been a challenge. Various techniques have been developed to address the detoxification of aqueous waste containing heavy metals, including adsorption, reverse osmosis, electrodialysis, chemical precipitation, membrane technologies, phytoremediation, ultrafiltration, ion exchange, and activated carbon, among others [11-15]. This work of research represents the worth of red mineral soil as a low cost and eco-friendly adsorbent for the adsorptive removal of Zn(II) from synthetic waste water.

Material and Methods

Collection of Samples

The red mineral soil was collected from Berinag regions of Pithoragarh district in Kumaun Hills of Uttarakhand.

Preparation of Adsorbent

The red mineral soil collected was filtered and air dried for a week in laboratory at room temperature. The dried soil then grinded by mixer grinder and sieved by 2 mm sieve to get desired size adsorbent particles. The physio-chemical properties of soil are determined by usual laboratory methods

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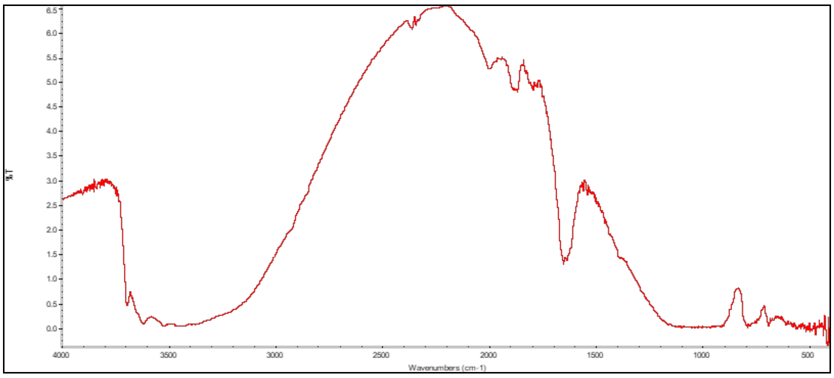
and standard techniques. The Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) characterization of red soil were performed. SEM analysis was conducted using a scanning electron microscope.



Graph 1: FTIR of Red Soil

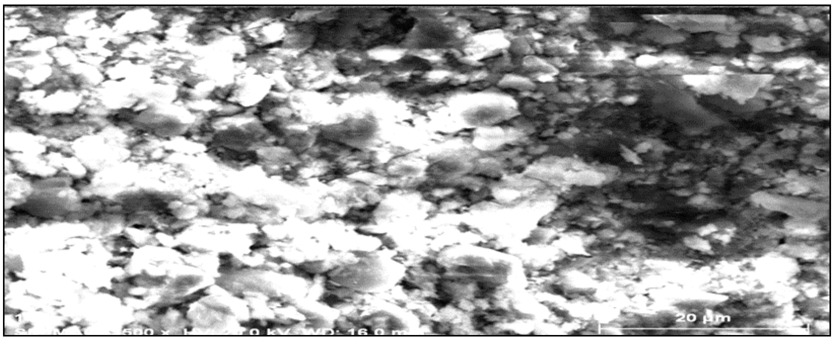
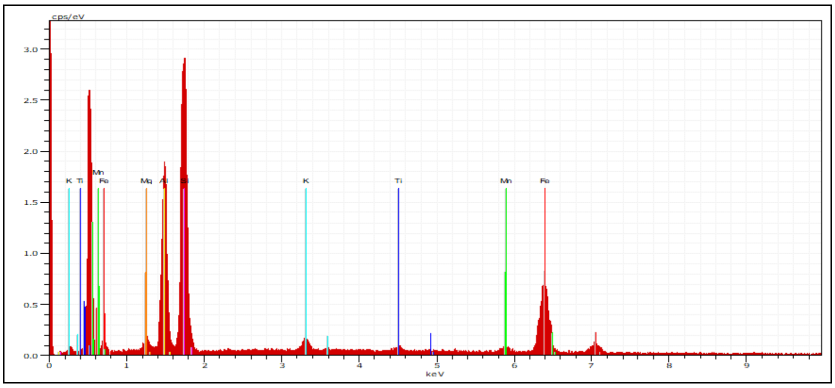


Fig 1: SEM image of Red Soil



Graph 2: Presence of metals in soil

Preparation of Synthetic Waste Water

The synthetic waste water was synthesized by preparing stock solution of Zn (II) by dissolving appropriate amount of Zinc salt $ZnSO_4$ in double distilled water. The pH of stock solution was adjusted by adding 0.1N HCL.

Adsorption Studies

The adsorption studies were performed using Batch equilibrium method to determine the amount of Zn (II) ion adsorbed by red mineral soil, influenced by contact time, temperature, pH, and adsorbent dosage. In a conical flask of 250 ml, a requisite amount of soil adsorbent was treated with synthetic waste water solution of known metal ion concentration (Analysed by AAS). The flask was regularly shaken for the desired contact time at a fixed revolution of 200 rpm for all the experiment.

The adsorption efficiency for metal ions was calculated by formula:

$$\text{Adsorption efficiency} = C_0\text{-}C_e/C_0 \;{*}100$$

Where C_0 and Ce are the initial and final (or equilibrium) metal ion concentrations respectively.

Adsorption Isotherm

The equilibrium relationship between the adsorbent and adsorbate is characterized by adsorption isotherms. In this study, the equilibrium data were analyzed using the Freundlich adsorption isotherm model.

Freundlich Isotherm Equilibrium:

Adsorption of Zinc (II) ions on heterogeneous surface of the red mineral soil follows Freundlich isotherm model. and this model can apply for multilayer adsorptions. The linear form of Freundlich isotherm can be written as-

$$\text{Log qe} = \log k_f + 1/n \log \text{Ce}$$

For the adsorption of Zinc (II) on the red mineral soil the logarithm values of qe (solute adsorbed per unit weight of adsorbent) and Ce equilibrium concentration.

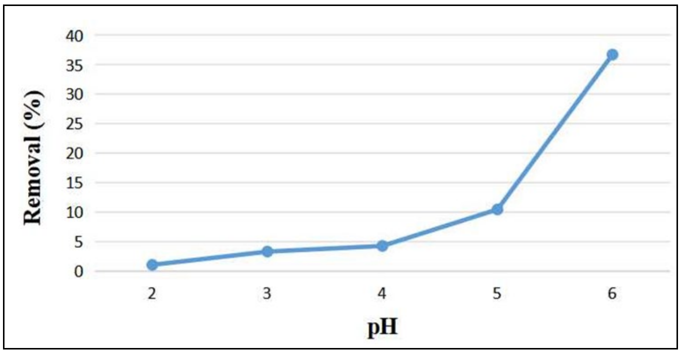
Results

Effect of pH of Solution

pH is one of the most important parameters affecting the adsorption process by different adsorbent. For the Zinc (II) ion adsorption, at presumed lowest pH 2 the removal efficiency is 1.03% and it increases slightly to 3.28% at pH 3. The increasing pH shows a gradual increase in the removal efficiency as it is 4.24% at pH 4, at pH 5 it reached to 10.44%. On increasing to pH 6 the removal efficiency of 36.73% was achieved. The graph 3, shows removal efficiency of soil adsorbent as a function of pH of solution for Zn (II) ions is in the table 1, which illustrate the adsorption of Zn (II) is increasing with increase in the pH value of working solution.

Table 1: Effect of solution pH on removal of Zn (II) ion onto red soil

Initial Metal Ion Concentration (mg/L)	Final Metal Ion Concentration (mg/L)	pH	Removal Efficiency (%)
10.00	9.897	2	1.03
10.00	9.672	3	3.28
10.00	9.576	4	4.24
10.00	8.956	5	10.44
10.00	6.327	6	36.73



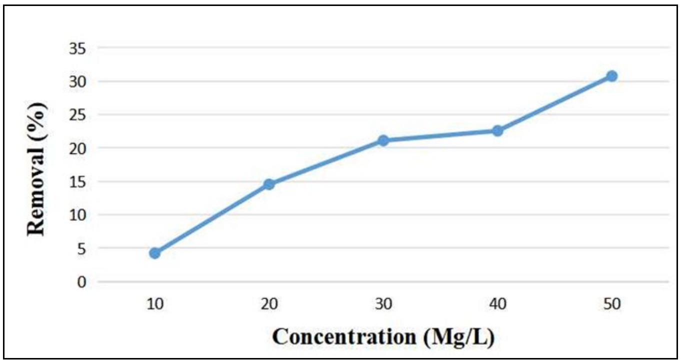
Graph 3: Effect of pH of solution

Effect of Zinc (II) Ion Concentration

The effect of metal ion concentration for Zinc(II) ion the removal efficiency is found 4.24% at 10mg/L metal ion concentration. The efficiency increases to 14.55% at 20mg/L concentration. With increase in concentration shows increase in efficiency as 21.11% at 30mg/L, 22.57%, at 40mg/L at 50mg/L adsorption efficiency to 30.77%. There is gradual increase in removal efficiency with rise in the temperature of adsorbent, may due to increase in rate of ion exchange reaction. But the small increase removal efficiency on high concentration is due to saturation of adsorbent sites. The removal efficiency of red soil adsorbent with variation of metal ion concentration for Zinc (II) is shown in graph 4.

Table 2: Effect of metal ion concentration on removal of Zn (II) ion onto red soil

Initial Metal Ion Concentration (mg/L)	Final Metal Ion Concentration (mg/L)	Removal Efficiency (%)
10.00	9.576	4.24
20.00	18.545	14.55
30.00	27.889	21.11
40.00	37.743	22.57
50.00	46.923	30.77



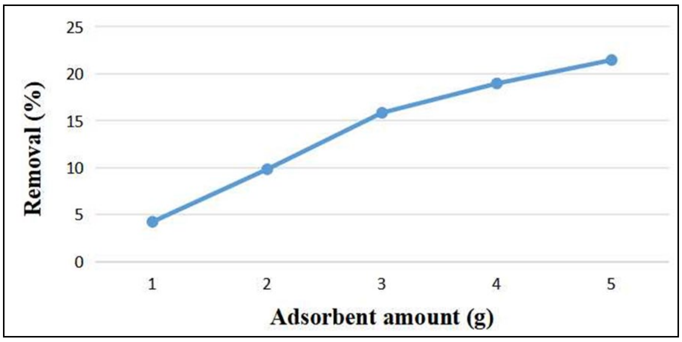
Graph 4: Effect of metal ion concentration

Effect of Adsorbent Dosage

Adsorbent dosage effect was studied by treating requisite adsorbent dosage (in g.) of red soil powder (1.0, 2.0, 3.0, 4.0 and 5.0) with 100 ml of working solution containing 10mg/L concentration of Zinc (II) at 200 rpm. The pH for these studies was adjusted to 4. After 20 minutes the adsorbent was filtered out and the filtrate is analysed for metal ion concentration by atomic absorption spectrophotometer. For Zinc (II) ion adsorption, 4.24% removal efficiency observed with 1 g adsorbent dosage and it increases to 9.84% with adsorbent dosage 2 g. The removal percentage further increases to 15.85% for 3 g, 18.97% for 4g of adsorbent. It reaches to maximum 21.47% at highest adsorbent dosage of 5 g. from graph 5 it is clear.

Table 3: Effect of adsorbent dosage on removal of Zn (II) ion onto red soil

Initial Metal Ion Concentration (mg/L)	Final Metal Ion Concentration (mg/L)	Adsorbent Dosage (g)	Removal Efficiency (%)
10.00	8.723	1	4.24
10.00	8.389	2	9.84
10.00	8.022	3	15.85
10.00	7.327	4	18.97
10.00	7.108	5	21.47



Graph 5: Effect of adsorbent dosage

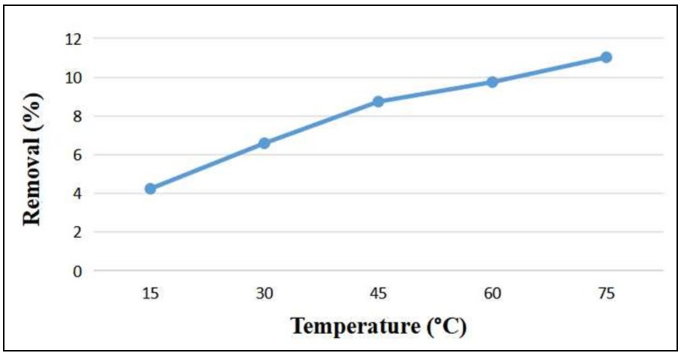
Effect of Temperature

The removal efficiency is found 4.24% at 15°C. The efficiency slightly increases to 6.59% at 30°C. Rising temperature shows increases in efficiency as 8.74% at 45°C, 9.75% at 60°C. At 75°C adsorption efficiency reached to 11.03%.

There is a gradual increase in removal efficiency with rise in the temperature may due to increase in ion exchange reaction. Graph 6 shows the gradual increase adsorption variation with temperature.

Table 4: Effect of temperature for removal of Zn (II) ion onto red soil

Initial Metal Ion Concentration (mg/L)	Final Metal Ion Concentration (mg/L)	Temperature (°C)	Removal Efficiency (%)
10.00	9.576	15	4.24
10.00	9.341	30	6.59
10.00	9.126	45	8.74
10.00	9.025	60	9.75
10.00	8.897	75	11.03



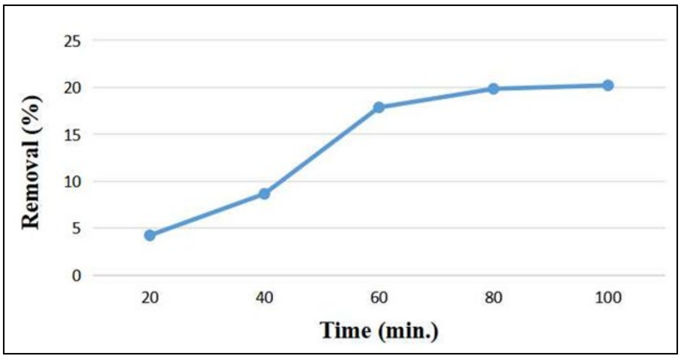
Graph 6: Effect of temperature

Effect of Contact Time

For Zinc(II) ion adsorption, the increase in contact time shows a regular improvement in the removal efficiency. The removal efficiency 4.24% is observed for 20 minutes and it increases to 8.66% for 40 minutes. The increasing contact time shows a regular increase in the removal efficiency as it is 17.87% for 60 minutes, for 80 minutes it reached to 19.85%. For contact time 100 minutes the 20.22% removal efficiency is obtained. The more interaction between the available binding sites and metal ions may be responsible for this trend of removal efficiency.

Table 5: Effect of Contact time for removal of Zn (II) ion onto red soil

Initial Metal Ion Concentration (mg/L)	Final Metal Ion Concentration (mg/L)	Contact Time (min)	Removal Efficiency (%)
10.00	9.576	20	4.24
10.00	9.134	40	8.66
10.00	8.213	60	17.87
10.00	8.015	80	19.85
10.00	7.978	100	20.22



Graph 7: Effect of contact time

Freundlich Adsorption Isotherm Studies

Adsorption of the metal ion on heterogeneous surface of the adsorbent follows the Freundlich isotherm model. Adsorption of Zinc metal ion on the red soil the logarithmic values of qe (solute adsorbed per unit weight of adsorbent) and Ce (equilibrium concentration of solute in solution) are given in table 6.

Table 6: Values of log Ce and log qe for Zinc onto red soil

Metal	Log qe (mg/g)	Log Ce (mg/L)
Zinc	-0.373	0.981
	0.163	1.268
	0.324	1.445
	0.353	1.577
	0.488	1.671

Value of KF (adsorption Capacity) of Zinc was 1.238, the adsorption intensity (1/n) was 0.787, and the regression value (R^2) in Freundlich isotherm equilibrium was 0.935.

Discussion

From the removal efficiency (%) result we got adsorption of Zn (II) onto red soil was highest at pH 6 i.e.; 36.73% and lowest at pH 2 i.e.; 1.03%, and in all parameters like temperature, adsorbent dosages, contact time and on metal ion concentration on increasing the values we have seen the removal efficiency gradually increasing.

Conclusion

Soil is a fundamental component of terrestrial ecosystems and is a highly complex, heterogeneous medium composed of the soil matrix, soil water, and soil air. Heavy metal ions are among the most toxic inorganic pollutants found in contaminated water, originating either from industrial activities or anthropogenic sources. Adsorption is a cost-effective process for their treatment in heavy metal polluted water. The primary interfaces involved in heavy metal adsorption in soils are predominantly inorganic colloids, such as clays and metal oxides.

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Author's Contributions: All authors contributed equally.

Conflicts of Interest: The authors affirm that they have no conflicts of interest.

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