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Removal of Heavy Metal Ions from Industrial Wastewater by Scolecite

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Abstract

It is a strategic target now to reuse treated industrial waste water for washing, irrigation etc., to efficiently manage and maximize Sudanese's water resources. The aim of the present work was to study the performance of natural zeolite (scolecite) for removing heavy metals from industrial waste water. Natural zeolite deposit sample was collected from Bayooda desert. Natural zeolite used (scolecite) was characterized by XRD, XRF, SEM and FTIR instruments. The physical properties (pH, EC, TDS, COD, BOD, total hardness) and chemical properties (Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe3+, Cr^{3+}) of the collected industrial waste water samples were investigated. Zeolite sorbed around 95.8, 88.1, 48, 50, 19.7 and 99.9% of Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+} and Cr^{3+} metal concentrations respectively. According to the percentage sorption values, the selectivity sequence of studied metals by natural zeolite can be given as $Cr^{3+}>Ni^{2+}<Pb^{2+}<Cd^{2+}<Zn^{2+}>Fe^{3+}$. These results show that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater.

Keywords: Scolecite; Industrial wastewater; Heavy metal ions

Introduction

Scolecite is a tectosilicate mineral belonging to the zeolite group; it is a hydrated calcium silicate, $CaAl_2Si_3O_{10}\bullet 3H_2O$. Only minor amounts of sodium and traces of potassium substitute for calcium. There is an absence of barium, strontium, iron and magnesium [1,2]. Scolecite is isostructural (having the same structure) with the sodium-calcium zeolite mesolite and the sodium zeolite natrolite, but it does not form a continuous chemical series with either of them [1]. It was described in 1813, and named from the Greek word, σκώληξ='worm' because of its reaction to the blowpipe flame. Scolecite is a common zeolite. It is a mineral of secondary origin, and occurs with other zeolites in the amygdaloidal cavities (cavities filled with secondary minerals) of weathered basalts, also in gneisses and amphibolites, and in laccoliths and dikes derived from syenitic and gabbroic magmas, and in contact metamorphic zones. It is a hydrothermal mineral derived from low temperature alteration of basalts and related rocks, associated with other zeolites, calcite, quartz and prehnite. It can be found on top of the calcium zeolites heulandites, stilbite and epistilbite [2]. Associated minerals include quartz, apophyllite, babingtonite, heulandite, stilbite and other zeolites. Due to their structural characteristics, natural zeolites can be used in several applications, from which Pansini [3] reviewed those of environmental interest. For example Zamzow et al. [4] used clinoptilolite to remove Al, Fe, Cu, and Zn from copper mine wastewater to below drinking water standards. Ouki and Kavannagh [5] showed that clinoptilolite and chabazite differ in their performance regarding capacity and selectivity. Other authors have demonstrated natural zeolites exhibit excellent selectivity a number of hazardous cations, a very moderate environmental impact [6-8]. The characteristics of industrial wastewater vary widely from industry to industry, and even within the same industry, depending on the raw materials used, processes employed, and various other factors [9]. Natural zeolites are especially attractive for removing heavy metal ions from effluent wastewaters mainly of industrial origin [5]. Zeolite media is a versatile product; it works the same way as any cation exchanger. Ca^{2+}, Mg^{2+} and heavy metals ions are replaced on one to one basis with sodium or potassium through the ion exchange process [11]. Our objective in this study is to investigate the removal of inorganic pollutants like Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+} and Cr^{3+} metal ions from a model solution by the scolecite natural zeolite (SNZ).

Materials and Methods

The sample of natural zeolite scolecite collected from Bayouda desert. It locates west of Kadabas, and south of Nubian Desert. The Bayouda volcanic field located:

Latitude: 18.330°18.20′0″N

Longitude: 32.75°32.45′0″E

There are four industrial wastewaters from:

1. Tannery in Khartoum.
2. Paints factory in Khartoum industrial area.
3. Petroleum water from Foloug field in Southern Sudan.
4. Mahmoud Sharif's electricity station. Samples collected and stored in one liter plastic container, and kept in refrigerator.

Chemicals

HCl (0.1M), NaCl (1M), sulfuric acid reagent (453.5 mL conc. H_2SO_4+5.5 g Ag_2SO_4), standard potassium dichromate (4.913 g $K_2Cr_2O_7$ in 167 mL H^2SO_4+33.3 g $HgSO_4$ and dilute to 1 Liter), standard ferrous ammonium sulfate (0.1M), ferrion indicator. Phosphate buffer, magnesium sulfate, calcium chloride, ferric chloride and manganese(II) sulfate solution. EDTA (4 g disodium salt in 500 mL distilled water and dilute to (1 Liter). Total hardness buffer solution. Total hardness indicator tablets.

Instruments

1. X-Ray diffract meter (XRD), system: Philips, Model: X-pert

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PRO stress XRD analyzer Cu-target radiation.

2. Atomic Absorption spectrophotometer (A.A.S); Perkin Elmer Model; 2380, flame double beam systems.

3. X-Ray Fluorescence (XRF) Model: ARL 9900 Series, Intelli power X-ray analyzer. Thermo Scientific, Belgium.

4. Infra-Red (IR) Spectrophotometer: Model: FTIR -8400S, Fourier Transform Infrared Spectrophotometer, Shimadzu.

5. Scanning Electron Microscope: Model: TESCAN. Oxford Instrument Company, using energy dispersive spectrometry (EDS) system.

6. Conductivity Meter: Model 4320 Jenway.

7. pH Meter: Model Corning Pinnacle 555 pH ion meter.

8. COD Reactor.

Method

A sample of (scolecite natural zeolite) 2 g as Na- Zeolite (315-500 µm) grain-size was placed in a beaker. Before determined concentrations of heavy metal ions from industrial wastewater samples, adjusted to decrease (pH) with Nitric acid. Then was added 50 mL industrial wastewater which had six heavy metal ions (Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, and Cr^{3+}) To facilitate extraction of the heavy metal ions. Stirring: vigorous shaking was applied for 10 min as contact time. The solution was then filtered at room temperature 25°C, and the filtrate was analyzed by (A.A.S) to determine the residual of the heavy metal ions concentration.

Results and Discussion

Results of scolecite were shown in Tables 1 and 2, the chemical composition of the natural zeolite as oxides. SiO_2 and AL_2O_3 percentage were found high in sample. This indicates that silicate and aluminate are important components in natural zeolites. Percentages of metal oxides ($Fe_2O_3^+$, CaO^+, MgO^+, Na_2O^+, K_2O) were found (32.31%) and this indicates that all cations were exchanged by Na^+ ions to form sodium zeolite as cation exchanger. The exchange of multivalent metal ions can be achieved in low pH to ensure the solubility of heavy metal cations according to Blanchard [11]. Characteristics of Scolecite were drown in Figures 1-3. The identification of the zeolite was carried by X-Ray diffract meter (XRD), system: Philips, Model: X-pert PRO stress XRD analyzer Cu-target radiation, used in the present work phase analysis was achieved by using XRD, sample was analyzed and found to be scolecite Figure 1. SEM photograph of zeolite particles is shown in Figure 2. It is clear that particles are rectangular in shape with sharp edges. In the infrared spectrum shown in Figure 3 of Scolecite without chemical processing but grinding as powder. It is reported the following positions of these bands: 462.88 cm^{-1} bending [O-Si(Al)O^+ Si-O-Al], 1029.9288 cm^{-1} stretching [Si(Al)O], 1645.17cm^{-1} [O-O] bond of water molecules bending (OH), and around 3423.41 cm^{-1} region stretching (OH).

Results of industrial wastewater: Samples were shown in Table 3. Physiochemical properties of industrial wastewater samples were drown in (Figure 4), Indicates pH for tannery wastewater (3.56), and pH for paints wastewater (8.40). In comparison the Arab Industrial Development and Mining Organization (AIDMO) standards (May 2001) where pH range [6-9], tannery wastewater is acidic, and paints wastewater is acceptable.

In comparison the AIDMO standards where the concentrations of total dissolved solids (TDS) does not exceed (1200 ppm), tannery wastewater (32100 ppm) has a very high value, where electricity wastewater (435 ppm) has acceptable value. This explains the high conductivity of tannery wastewater (53.100 µs/cm).

In comparison the AIDMO standards for biological oxygen demand BOD (30 ppm), tannery wastewater has a high value (53.34 ppm), while and paints wastewater is acceptable (7.5 ppm). Chemical oxygen demand (COD) in tannery wastewater (3000 ppm), and petroleum wastewater (112 ppm) are high in comparison the AIDMO standards (10 ppm). Total hardness in tannery wastewater is 1012.78 ppm, but it is much lower in petroleum wastewater (34.56 ppm). High concentrations of heavy metal ions were shown in Table 4. Thus it is concluded that tannery wastewater has many pollutants discharged directly without treatment to the river. Removals of heavy metals by scolecite were drowning in used SPSS IBM version 20 were shown in

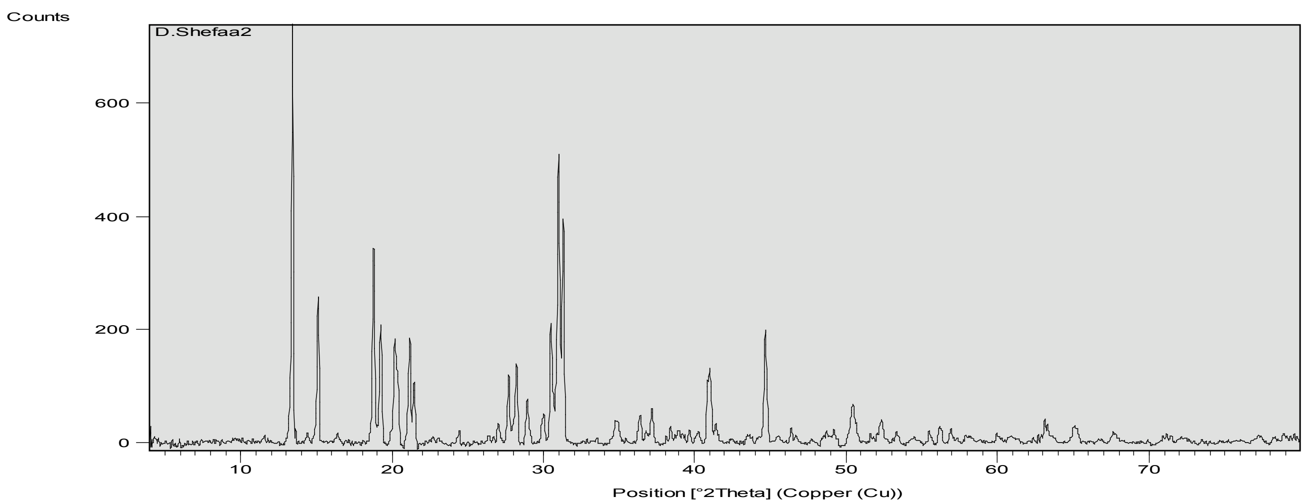

Figure 1: XRD Patterns for scolecite zeolite.

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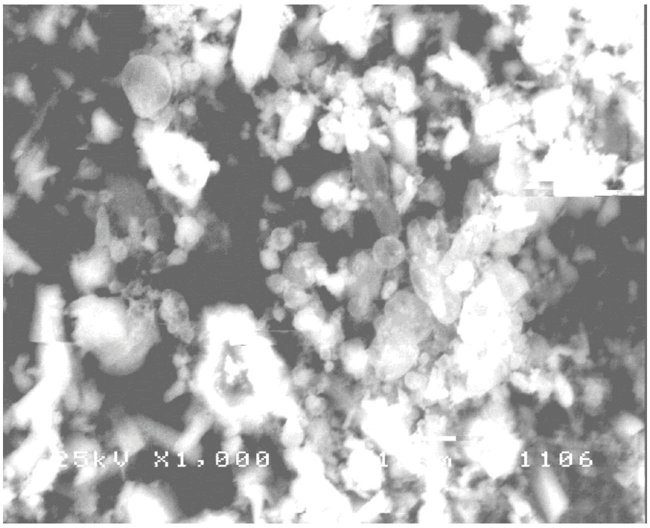

Figure 2: Show SEM image for scolecite.

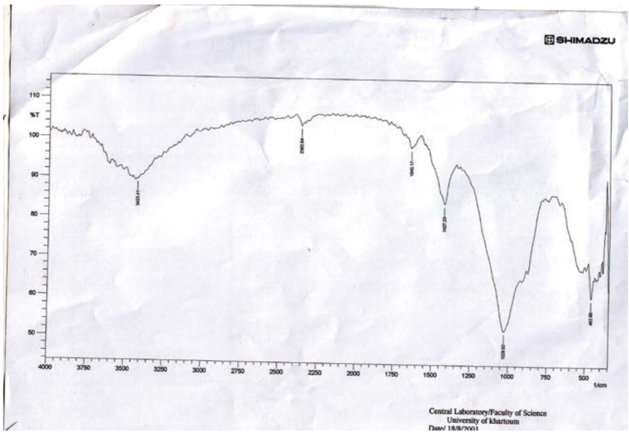

Figure 3: I.R for scolecite.

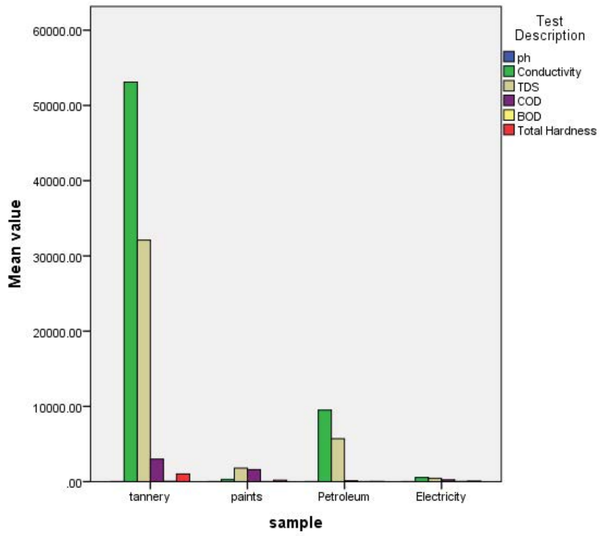

Figure 4: Show physiochemical properties results of industrial wastewater.

Characteristic	Sources
Physical properties	
Color	Domestic and industrial wastes, natural decay of organic materials.
Solids	Domestic water supply, domestic and industrial wastes, soil erosion, inflow, and infiltration.
Chemical constituents	
Heavy metals	Industrial wastes.
pH	Domestic, commercial, and industrial wastes.
Nitrogen	Domestic and agriculture wastes.
Sulfur	Domestic water supply, domestic, commercial and industrial wastes.
Methane	Decomposition of domestic wastes.
Archaebacteria	Domestic wastes, surface water infiltration, treatment plants.

Table 1: Physical, chemical, and biological characteristics of wastewater and their sources [10].

Component (%)	Scolecite (%)
SiO_2	43.48
AL_2O_3	12.98
Fe_2O_3	10.07
CaO	11.82
MgO	6.08
Na_2O	2.59
K_2O	1.75
SO_3	0.00
Cl	0.114
LOI	11.12

Table 2: Chemical composition of scolecite by XRF.

Waste Water test	Tannery wastewater	Paints wastewater	Petroleum wastewater	Electricity wastewater
pH	3.56	8.40	7.58	8.04
Conductivity	53100 μs/cm	299 μs/cm	9500 μs/cm	544 μs/cm
TDS	32100 ppm	1807 ppm	5710 ppm	435 ppm
BOD	53.34 ppm	7.5 ppm	9.65 ppm	27.7 ppm
COD	3000 ppm	1600 ppm	112 ppm	250 ppm
Total hardness	1012.78 ppm	184.79 ppm	34.56 ppm	74 ppm

Table 3: Physiochemical properties for industrial wastewater.

Wastewater Heavy metals	Tannery wastewater ppm	Paints wastewater ppm	Petroleum wastewater ppm	Electricity wastewater ppm
Ni^{2+}	20.0	4.0	2.25	0.923
Pb^{2+}	1.26	3.67	3.89	4.882
Zn^{2+}	1.23	0.095	0.003	0.00
Cd^{2+}	7.40	0.001	0.00	0.00
Fe^{3+}	1.83	0.014	0.00	0.020
Cr^{3+}	6000.0	5.62	0.35	11.785

Table 4: Concentrations of heavy metal ions in industrial wastewater by AAS

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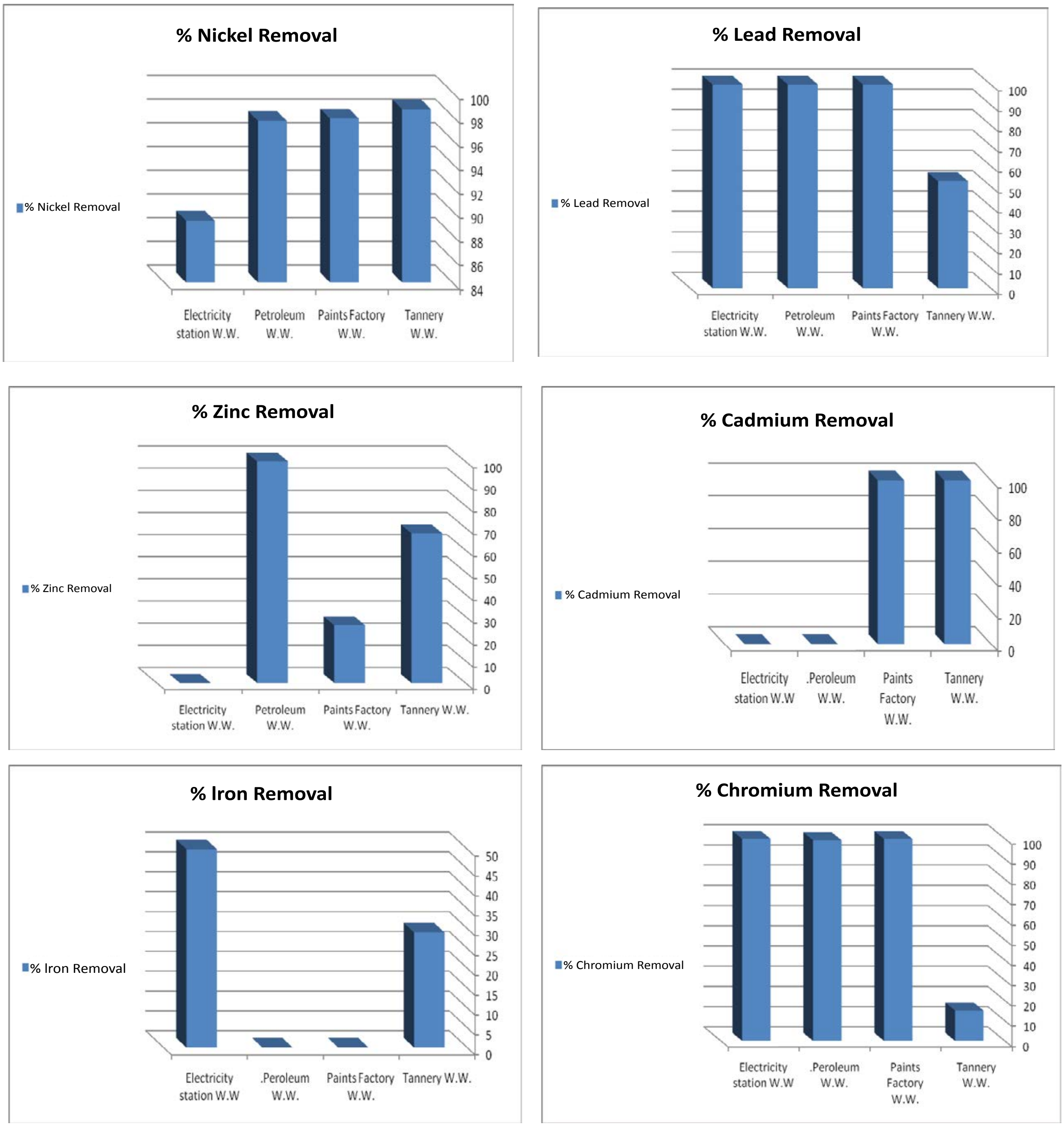
Table 5. Scolecite removed 95.8, 88.1, 48, 50, 19.7 and 99.9% of Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+} and Cr^{3+} metal concentrations respectively. According to the percentage removal values, the selectivity sequence of studied metals by scolecite can be given as $Cr^{3+}>Ni^{2+}<Pb^{2+}<Cd^{2+}<Zn^{2+}>Fe^{3+}$ (Figure 5). These results show that scolecite hold great potential to remove cationic heavy metal species from industrial wastewater.

Conclusion

In the present study, we characterized industrial wastewater effluents, results indicated that many toxic pollutants drained directly to river and affected dangerously to environment. Scolecite natural zeolite is capable of removing metal ions Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Cr^{3+} from industrial waste water samples. The percentage of removal heavy metal ions by scolecite 95.8, 88.1, 48, 50, 19.7 and 99.9% of Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+} and Cr^{3+}. The obtained results showed that natural zeolite can be used effectively for the removal of these metal ions from industrial wastewater. This naturally occurring material provides a substitute for the use of other materials as adsorbent due to its availability and its low cost.



Figures 5: Six heavy metals removal by scolecite.

Heavy metal ions	sample	Mean	Std. Deviation	N
Ni^{2+}	tannery	98.6	.	1
	paints	97.8	.	1
	Petroleum	97.6	.	1
	Electricity	89.2	.	1
	Total	95.8	4.42116	4
Pb^{2+}	tannery	52.4	.	1
	paints	100	.	1
	Petroleum	100	.	1
	Electricity	100	.	1
	Total	88.1	23.8	4
Zn^{2+}	tannery	67.5	.	1
	paints	26	.	1
	Petroleum	100	.	1
	Electricity	0	.	1
	Total	48.375	44.24058	4
Cd^{2+}	tannery	99.9	.	1
	paints	100	.	1
	Petroleum	0	.	1
	Electricity	0	.	1
	Total	49.975	57.70617	4
Fe^{3+}	tannery	29	.	1
	paints	0	.	1
	Petroleum	0	.	1
	Electricity	50	.	1
	Total	19.75	24.36357	4
Cr^{3+}	tannery	15	.	1
	paints	99.8	.	1
	Petroleum	99.2	.	1
	Electricity	99.9	.	1
	Total	78.475	42.3178	4
Total	tannery	60.4	35.15969	6
	paints	70.6	45.37559	6
	Petroleum	66.1333	51.23416	6
	Electricity	56.5167	47.4802	6
	Total	63.4125	42.5116	24

Table 5: Descriptive statistics of scolecite - Dependent variable: % removal.

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