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Schiff Bases and Their Ability to Remove Heavy Metals

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Abstract
The presence of heavy metals in water has been an increasing source of concern on a global scale. Hence the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated a worldwide research interest. This study investigates the efficacy of the removal of toxic heavy metal ions, chromium (Cr^{3+}), and copper (Cu^{2+}) by adsorption to a Schiff base of salicylaldehyde and aniline. The adsorption process was studied with respect to contact time and Infra-red (IR) spectral analysis was carried out before and after extraction to indicate possible adsorption of metal ions to the Schiff base. The result showed that adsorption was reached within 10 and 15 minutes respectively. 72.5 percent of chromium was observed to be the maximum removal percentage while 99 percent of copper was also observed to be the maximum removal percentage. Therefore, it is deduced that the Schiff base of salicylaldehyde and aniline removes copper more efficiently than chromium with a shorter time duration.

Keywords*: Heavy metals, Wastewater, Adsorption, Schiff base.*

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I. Introduction

Heavy metal pollutants of wastewater are notable environmental contaminants and their toxicity is a problem of increasing global concern for environmental, ecological, and nutritional reasons [1]. Many industries such as electroplating, pigments, metallurgical processes, mining, and leather industries release various concentrations of heavy metals. Despite stringent regulations restricting their reckless disposal, these metal ions may still surface in a variety of wastewaters originating from catalysts, electrical apparatus, painting and coating, extractive metallurgy, antibacterial, insecticides and fungicides, photography, pyrotechnics, smelting, metal electroplating, fertilizer, mining, pigments, stabilizers, alloy industries, electrical wiring, plumbing, heating, roofing, and construction piping, water purification, gasoline additives, cable covering, ammunition and battery industries, and sewage sludge [2–4]. Recently, special consideration has been given to the environmental pollution with heavy metal ions because of their high toxicity and non-biodegradability. They have industrial, agricultural, medical domestic, and technological applications. Exposure of humans to heavy metal contaminants as well as public solicitude for the related health risks have both escalated dramatically as a result of an exponential increase of their use in these various applications. Environmental exposure to high concentrations of heavy metal contaminants has been linked with various cancers and kidney damage.

Heavy metal pollution in water is elevated in areas where mining, smelters, metal processing refineries, wood preservation, and paper processing facilities are situated. The most commonly found heavy metal contaminants in wastewater include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks to human health and the environment [5]. The commonly used procedures for removing metal ions from effluents include filtration [6], chemical precipitation [7], chemical coagulation [8], flocculation [9], ion exchange [10], reverse osmosis [11], membrane technologies [12–14], and solvent extraction [15]. However, these methods are limited by high operational cost and/or may also be inefficient in the removal of some toxic metal ions, mainly at trace level concentration [16], hence the need for more economical and safe methods for heavy metal removal.

Schiff bases are organic compounds that have an azomethine group (-CH=N -). These bases are often formed by condensation of a carbonyl compound with a primary amine [17]. A significant number of Schiff base complexes are of potential biological interest, being used as more or less successful models of biological compounds [18]. They played a formative role in the development of modern coordination chemistry and can be found at key points in the development of inorganic biochemistry, optical materials, and catalysis [19]. This present work studies a Schiff base derived from salicylaldehyde and aniline and its ligand ability to remove chromium and copper ion from a bi-metal system wastewater).

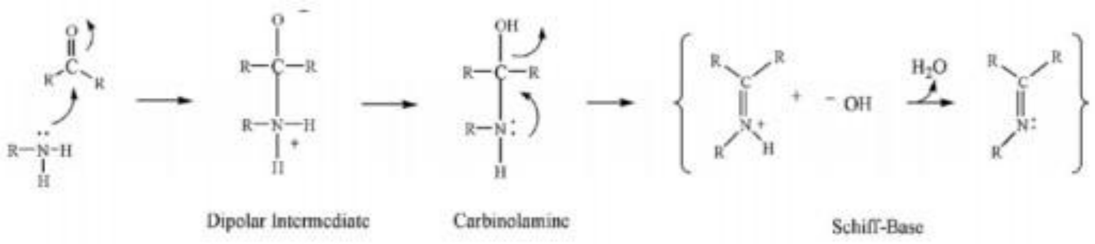

Figure 1: Mechanism of formation of Schiff base

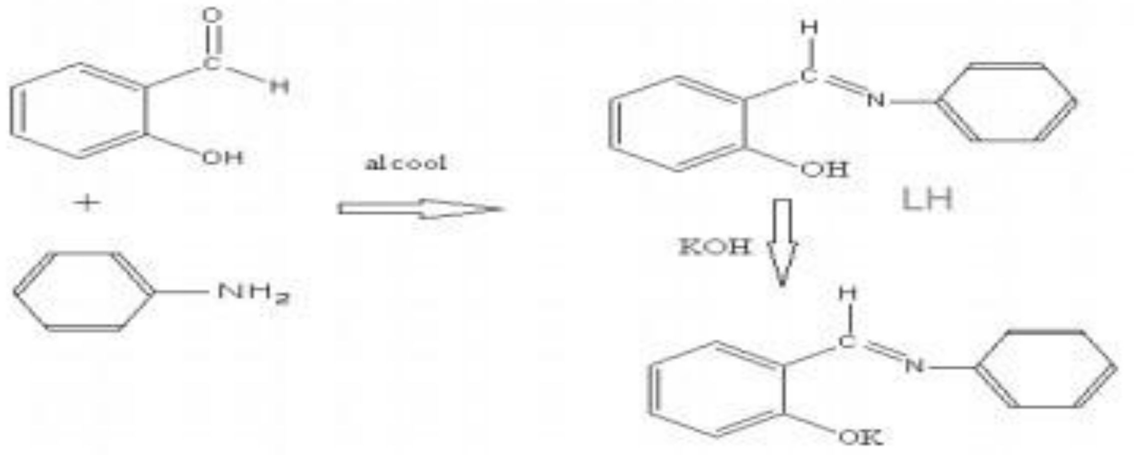

Figure 2: Schiff base of Salicylaldehyde and aniline

II. Materials and Methods

Materials

The Schiff base was synthesized by adding 0.1711 moles (20.8875g) of salicylaldehyde and 0.1711molese (15.913g) of Aniline to a beaker alongside 10ml of absolute ethanol and a drop of 5% HCL solution. The mixture was gently refluxed for an hour, then another 10ml of absolute ethanol was added. The mixture was transferred to a new beaker and was allowed to cool in a water bath. A crystal was fully formed, the product was filtered and recrystallized.

Solubility Study

0.5g of the Schiff base was dissolved in 5ml of the following solvents: benzene, chloroform, acetyl acetone, propan-2-ol, ethanol, and diethyl ether.

Thin Layer Chromatography Test

A thin layer chromatography test was carried out using propan-2-ol as a solvent and a capillary tube to spot the chromatographic plate, Iodine fuming was also used to boost visibility by putting the chromatographic plate in a glass jar with iodine crystals for 1 hour.

Melting Point Test

The melting point test was carried out on the Schiff base by; filling a capillary tube with the Schiff base, the capillary tube was then attached to a thermometer using a tape, and the thermometer was submerged into a hot paraffin oil heated to a certain temperature, The Schiff base was observed to melt and the reading was taken.

Synthetic Wastewater

Metal solutions of (Cu, Cr) were prepared by dissolving 0.19g of Copper (II) nitrate tetrahydrate and 0.256 g of Chromium (III) chloride Pentahydrate separately in 500ml of distilled water to result in known concentrations of the metal ions required and to make synthetic wastewater, 200ml of each of the resulting solutions were introduced into a 1000ml beaker stirred properly to give the bi-metal system. The pH of the bi-metal system was determined to be 4.2 using a portable pH Meter.

Extraction Procedure

50ml of adsorbate (equimolar bi-metal system) was introduced into 6 beakers labeled 1 through 6. 0.5 g of adsorbent (Schiff base) was introduced into each beaker followed by mild stirring to frequently change the contact area. Beaker 1 was stirred for 5 minutes, beaker 2 for 10 minutes, beaker 3 for 15 mins beaker 4 for 20 minutes, beaker 5 for 25 minutes beaker 6 for 30 minutes. After each time, the mixture is filtered and the filtrate is collected in sample bottles labeled 1 through 6 corresponding to their respective time. The filtrate was then taken for atomic absorption spectrophotometer (AAS) for analysis, and I.R identification was carried out on the Schiff base residue.

III. Results and Discussion

Solubility Study

The Schiff base was observed to be soluble in some of the solvents listed below and the following results were obtained.

Table: 1: Solubility test result

SOLVENT	**SOLUBILITY**
BENZENE	SOLUBLE
CHLOROFORM	SOLUBLE
ACETYLACETONE	SOLUBLE
PROPAN 2 OL	SPARINGLY SOLUBLE
ETHANOL	NOT SOLUBLE
DIETHYLETHER	SOLUBLE

Melting Point Test

The sample (Schiff base) was observed to melt at 49◦C, which implies that the sample is pure.

Thin Layer Chromatography (TLC) Test

The sample had a uniform fluid flow on the silica gel paper, also only one color was observed on the paper which indicates that the sample is pure.

Figure 3: Chromatography Silica Gel Paper

AAS Adsorption Result

AAS analysis of the bi-metal solution after removal of chromium and copper metals gave the following results at different time intervals, which are; 5, 10, 15, 20, 25, and 30 minutes respectively:

For chromium:

Table 2: Amount of chromium removed over time

TIME(MINS)	**INITIAL CONCENTRATION [mg]**	**FINAL CONCENTRATION [mg]**
5	10	4.25
10	10	3.04
15	10	2.75
20	10	3.243

25	10	5.30
30	10	6.50

Percentage Removal of Chromium

The percentage removal of chromium ion:

$(C_o - C_e)\ C_o$

$\% Removal = \underline{\qquad\qquad} \times 100 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots eq$ 4.1

C_o = Initial concentration

C_e = Final concentration

Table 3: percentage removal of chromium

TIME(MINS)	% REMOVAL
5	57
10	69.6
15	72.5
20	67.57
25	47
30	35

Graph of Percentage Removal of Chromium against Time

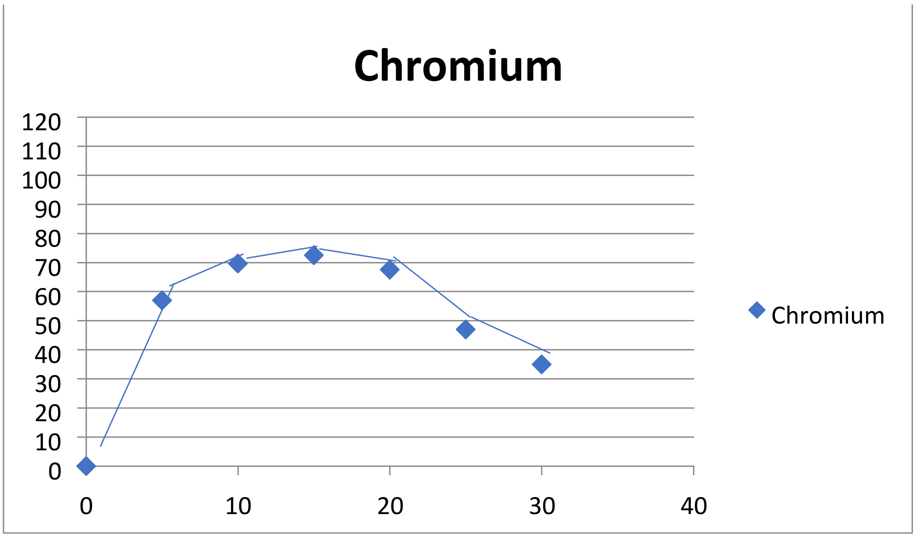

Figure 4: graph of chromium % removal against time

Effect of Contact Time on Chromium Removal

As seen in figure 4.2 above, the percentage removal was studied at a constant temperature, pH, and weight of the samples (Schiff base and bi-metal system), this parameter was varied from 5 to 30 minutes. From figure 5 the percentage removal is seen to increase with increasing contact time for about 15 minutes, and then a decline sets in. This confirms that there is adsorption between the Schiff base and chromium ion in the bi-metal solution. The highest percentage removal was achieved at 72.5%. That makes 15 minutes the maximum recovery time, hence can be considered as the maximum adsorption value.

For copper

Table 4: Amount of copper removed over time

TIME(MINS)	INITIAL CONCENTRATION [mg]	FINAL CONCENTRATION [mg]
5	10	0.34
10	10	0.18
15	10	0.24
20	10	0.60
25	10	0.86
30	10	2.0

Percentage Removal of Copper

The percentage removal of copper ions was calculated using:

$(C_o - C_e)\ C_o$

$\%\ Removal = \underline{\hspace{3em}} \times 100 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots\ eq\ 4.1$

C_o = Initial concentration

C_e = Final concentration

Table 5: percentage removal of copper

TIME(MINS)	% Removal
5	96.9
10	99
15	97.6
20	94
25	91.4
30	80

Graph of Percentage Removal of Copper against Time

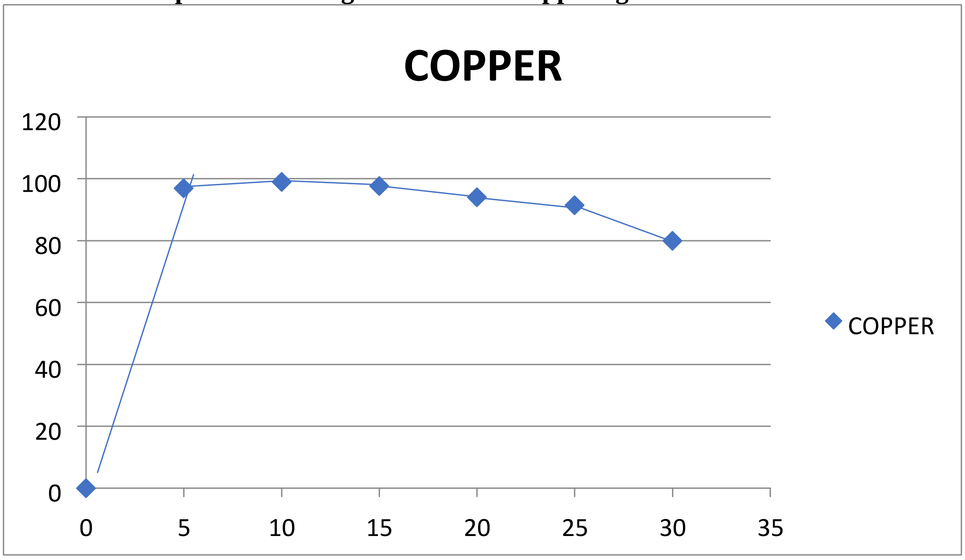

Figure 5: graph of chromium % removal against time

Effect of Contact Time on Copper Removal

As seen in figure 4.3 above, the percentage (%) removal was studied at a constant temperature, pH, and weight of samples (Schiff base and bi-metal system), this parameter was varied from 5 to 30 minutes. From figure 6 the percentage removal is seen to increase with increasing contact time for about 10 minutes, and then a decline sets in. This confirms that there is adsorption between the Schiff base and copper ion in the bi-metal solution. The highest percentage removal was achieved at 99%. That makes 10 minutes the maximum recovery time, hence can be considered as the maximum absorption value.

Comparison between Chromium and Copper Metal

Table 6: Comparison between Chromium and Copper Metal Removal over Time

Time (Mins)	Initial Concentration (Mg)	Final Concentration Chromium (Mg)	Final Concentration Copper (Mg)
5	10	4.25	0.34
10	10	3.04	0.18
15	10	2.75	0.24
20	10	3.243	0.60
25	10	5.3	0.86
30	10	6.5	2.0

Table 7: % removal of chromium and copper

Time (Mins)	%Removal Chromium	%Removal Copper
5	57	96.9
10	69.6	99
15	72.5	97.6
20	67.52	94
25	47	91.4
30	35	80

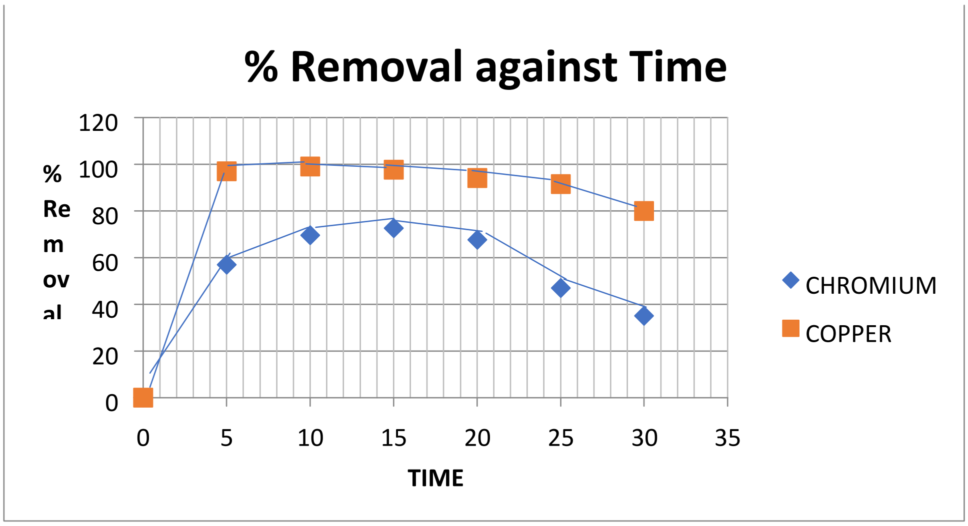

Figure 6: comparison graph of chromium and copper against time.

IV. IR Analysis

The synthesized compounds were subjected to Ft-IR for possible identification. The IR results of the ligands and that of their complexes are shown in Table 4.8

Table 8: Significant bands of FT-IR spectral results

SYMBOL	**v(C=N)**	**v(C-O)**	**v(C=C)**	**v(M-N)**	**v(M-O)**
L	**1607.72**	**1274.03**	**1576.88**	**748.41**	**686.86**
HL	**1609.65**	**1275.95**	**1578.79**	**758.05**	**688.61**

As shown in Table 4.8, vibrations of the Imine C=N group were observed at 1607.72 indicating the formation of ligand. Band peak at 1578.79 is assigned to v(C=C) vibration of aromatic structure and 1270.03 is assigned to the phenolic group. After Complexation upon coordination with metal ions there is a shift C=N band to 1609.65. Bands at 748.41 and 688.61 can be attributed to M-O & M-N stretching mode.

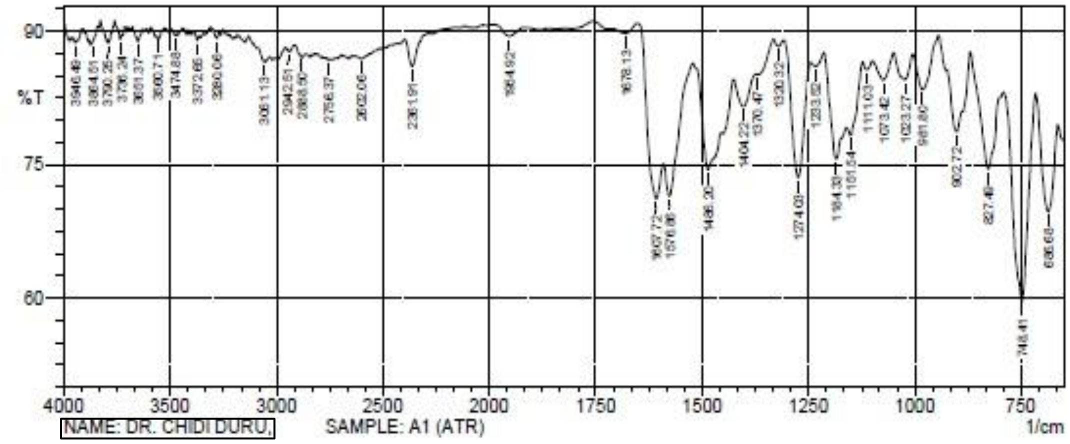

FIG 7: FT-IR Chart of Schiff Base

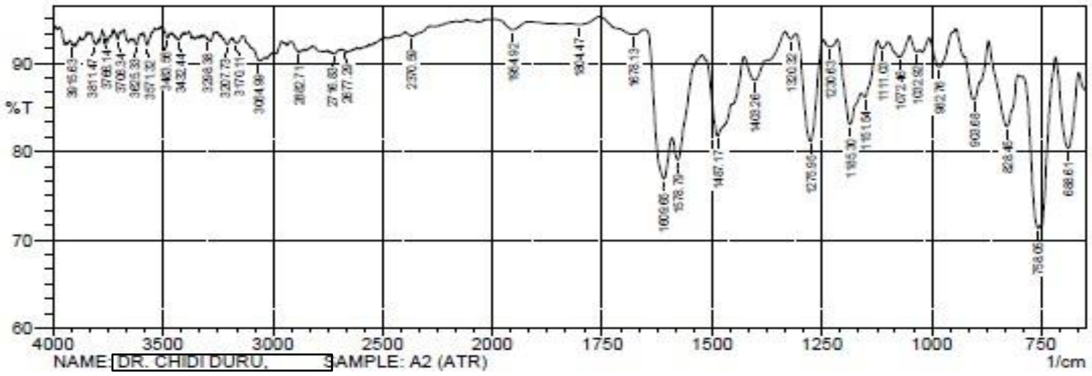

FIG 8: FT-IR Chart of Schiff Base after Extraction

V. Conclusion

1. The Schiff base was more efficient at removing copper (II) ions from the bi-metal system than chromium (III) ions. Considering the result from the AAS study 0.18mg of copper ions was left in the bi-metal solution at the point of maximum adsorption while 3.04mg of chromium was left in the bi-metal solution at the point of maximum adsorption after extraction.
2. The Schiff base had a higher percentage removal of copper with 99% of the metal removed than chromium which had maximum percentage removal of metal ions at 72.5%.
3. Copper metal achieved maximum metal ion removal faster than chromium at around 10 minutes when compared to chromium metal with 15 minutes.

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