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Removal of Heavy Metals using Combination of Adsorbents - A Case Study using Industrial Waste Water

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Abstract

Heavy metals are widely used in numerous industries such as paints and pigments, glass production, mining operation, electroplating, battery manufacturing and textile industries. The significant losses of heavy metals occur during the manufacturing processes and these lost heavy metals are discharged in the effluent. As they move from one ecological trophic level to another, metallic species start damaging the ecosystem. They also become difficult to track as they move up in trophic levels. They accumulate in living tissues throughout the food chain. Due to biomagnification, humans receive the maximum impact, since they are at the top of the food chain. Hence heavy metal contamination has been a critical problem. Adsorption of heavy metals is one of the techniques for treatment of waste water containing different types of selected heavy metals. In this study, the adsorbents Coconut shell, Rice husk, Water Hyacinth, Shrimp Shells and Crab shells are investigated as viable materials for removal of Heavy metals. The effect of contact time, particle size and adsorbent dosage are studied. The aim of this study is to use water hyacinth as an adsorbent in removing heavy metal content from industrial waste water and to use the above mentioned adsorbents in combination to see the effect of adsorption. The metal concentrations are determined using Atomic Absorption Spectroscopy. The adsorbents are pretreated by way of cleaning, washing, sun drying and then crushing to obtain particles in different size ranges in order to study the effect of different parameters on the adsorption. The main objective of this project is to use cheap and readily available solid wastes such as Coconut Shell, Rice Husk, Water Hyacinth, Shrimp Shells and crab shells as adsorbents for the removal of heavy metals from the industrial waste water, and to test the effect of contact time, particle size and adsorbent dosage on the extent of adsorption.

Keywords: *Adsorption, Shrimp shell, Combination of adsorbents*

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INTRODUCTION

In the past century there has been a rapid expansion in industries. This has lead to an increase in the complexity of toxic effluents. Several industrial processes generate metal containing wastes. Heavy metal contamination has been a critical problem mainly because metal tend to persist and accumulate in the environment. Copper, nickel, mercury, lead, zinc, arsenic, chromium, cadmium etc. are such toxic metals which are being widely used. They are generated by the dental operation, electroplating, tanning, textile, paper and pulp industry and are potentially toxic to humans. These heavy metals are used in many industries for different purposes and released to the environment with the industrial wastage. Therefore, the effluents being generated by these industries are rich in heavy metals and should be treated before being discharged into the common waste water.

On the other hand aquatic systems are particularly sensitive to pollution possibly due to the structure of their food chain. In many cases harmful substances enter the food chain and are concentrated in fish and other edible organisms. As they move from one ecological trophic level to another, metallic species start damaging the ecosystem. They also become difficult to track as they move up in trophic levels. They accumulate in living tissues throughout the food chain. Due to biomagnification, humans receive the maximum impact, since they are at the top of the food chain. Hence heavy metal contamination has been a critical problem.

The efficient removal of toxic metals from waste water is an important matter and it is being studied. A number of technologies have been developed over the years to remove toxic metal from waste water. Physical treatment can also be used to remove small concentration of hazardous substances dissolved in water that never settles out. The current physico-chemical processes for heavy metal removal like precipitation, reduction, ion-exchange etc. are expensive and insufficient in treating large quantities. They also cause metal bearing sludge which is difficult to dispose off. Some of these traditional methods are also extremely expansive, thereby proving uneconomical, especially for developing countries where large volumes of these wastes are generated. Therefore, there is a requirement for a newer and effective method which is also cost-effective and environment friendly.

One of the most commonly used techniques involves the process of adsorption, which is the physical adhesion of chemicals on to the surface of solid. Recently, efforts have been made to use cheap and readily available agricultural wastes such as coconut shells, orange peel, rice husk, peanut husk and saw dust as adsorbents to remove heavy metals from waste water.

This work focuses on treatment of industrial waste water containing heavy metals using different adsorbents like coconut shell, rice husk, water hyacinth, shrimp shells and crab shells in combination. The main objectives are:

1. Removal of heavy metals from waste water using different adsorbents in combination.
2. Removal of heavy metals from waste water using water hyacinth as the adsorbent.
3. Optimization of various adsorption parameters like time of contact, particle size and adsorbent dosage.
4. Plotting of adsorption isotherms.

MATERIALS AND METHODS

The aim of this study was to use water hyacinth as an adsorbent in removing heavy metal content from industrial waste water and to use the other adsorbents in combination to see the effect of adsorption [1–9].

The adsorbents used for this project were as follows:

1. Rice Husk
2. Coconut Shell
3. Shrimp Shells
4. Crab Shells
5. Water Hyacinth

The adsorbents were obtained from different sources. They were cleaned using tap water to eradicate possible strange materials present in it (dirt and sand). Washed sample material was sun dried for 2–5 days and then crushed using ball mill to reduce the size. The particle sizes chosen were 100, 150 and 250 microns (Figures 1 and 2).

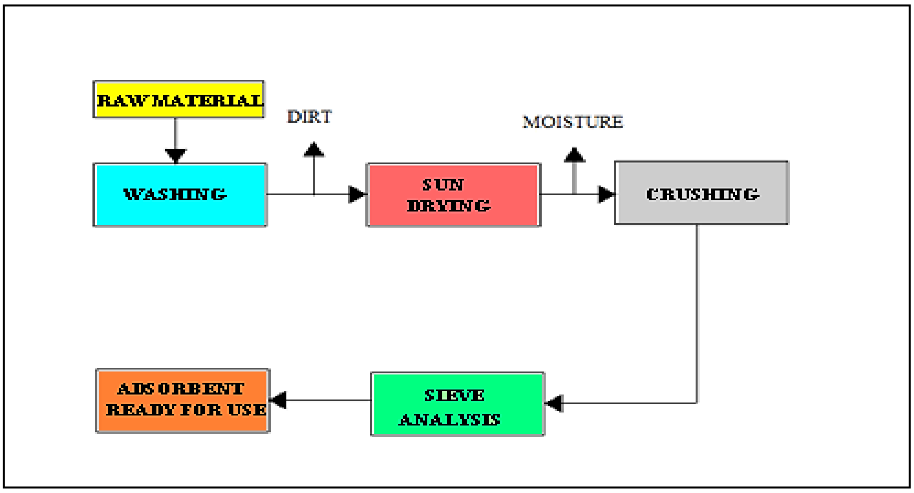

Fig. 1: *Flow Diagram for Pretreatment of Adsorbents.*

Fig. 2: *Pretreated Coconut Shell and Rice Husk.*

Among the above mentioned adsorbents, only the first four adsorbents were used in combination with each other. This is because already extensive research has been carried on the use of these materials as adsorbents for the removal of heavy metal contents from waste water. However, the effect of water hyacinth, as an adsorbent to remove the heavy metals from industrial waste water has not been fully explored yet. Therefore, the effect of water hyacinth as an adsorbent was tested individually and not in combination with the other adsorbents. Most of the other studies that have been carried out so far, involve sun drying as well as activating the adsorbents by heating it to typical carbonizing temperatures of about 400°C and then activating them by heating it to temperatures of about 700°C. However, in this study the effect of these natural adsorbents without having the need to activate them is studied.

Industry Waste Water Sample

The waste water was collected from the effluent discharge point of an electroplating industry. It was carefully bottled in a plastic container and was immediately taken to a laboratory for analysis.

The heavy metals present in the waste water sample were analyzed using atomic absorption spectrometer (AAS) (Biotechnology center, Government of Karnataka) [10]. It detected the concentration of Cr, Zn, Pb and Cd. The initial concentration of the metal ions present in the waste water is shown in the Table 1.

Table 1: *Initial Metal Concentration of the Untreated Industrial Waste Water.*

Heavy metal	Initial concentration (ppm)
Zn	5246
Cr	100.823
Pb	0.236
Cd	0.006

Adsorption Study

The adsorbents were mixed in different proportions as shown in the Table 2.

Table 2: *Combination of Adsorbents in Different Proportions.*

Rice Husk (%)	Coconut Shell (%)	Shrimp Shells and crab shells (%)
25	25	50
25	50	25
50	25	25

Adsorption experiment was done by measuring 100 ml of waste water and poured into a 250 ml conical flask (Figure 3). 2 g of adsorbent mixture of different proportions as shown in Table 2 was added to the waste water sample. The conical flask containing the waste water and adsorbent mixture was placed in a wrist shaker at room temperature for a period of 200 min. The suspension was filtered. Atomic absorption spectroscopy (AAS) was used to analyze the concentration of different metal ions present in the filtrate (Figure 4).

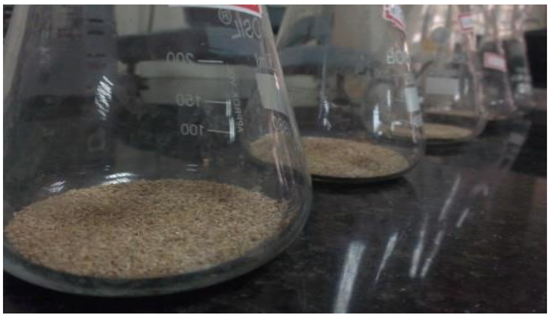

Fig. 3: *Adsorbent Mixture.*

Effect of Contact Time

The effect of contact time on removal of metal ions was studied for the maximum period of 200 min. 2 g of the adsorbent mixture was added to different conical flasks containing 100 ml of waste water and placed in a wrist shaker and agitated for each of the different contact time chosen (40,80,120,160 and 200 min). The content of each flask was filtered and analyzed after each agitation time.

Effect of Adsorbent Dosage

Different dosages of the adsorbent mixture (2, 3.5 and 5 g) were added in different conical flask containing 100 ml of waste water and agitated in a shaker at room temperature. The content of each flask is then filtered and analyzed after the agitation time (Figure 4).

Effect of Particle Size

Particle size was varied from 100 to 250 microns (100, 150 and 250 microns) to study the effect of particle size on adsorption of metal ions. 2 g of the adsorbent mixture was added to different conical flasks containing 100 ml of waste water and placed in a wrist shaker. The content of each flask was then filtered and analyzed after the agitation time.

Fig. 4: *Waste Water Sample after Adsorption.*

RESULTS AND DISCUSSION

Composition 1: 50% shrimp shell: 25% rice husk: 25% coconut shell

Effect of Contact Time on Adsorption

Volume of waste water: 100 ml
Adsorbent dosage: 5 g
Particle size: 100 micrometer (Table 3)

Table 3: *Concentration of Heavy Metal after Adsorption for Adsorbent Dosage of 5 g and 100 micrometer Particle Size.*

Sl. No	Contact Time (min)	Concentration of metal remained (ppm)	
		Zn	Cr
1	40	0.10	0
2	80	0.17	0
3	120	0.23	0
4	160	0.19	0
5	200	0.19	0

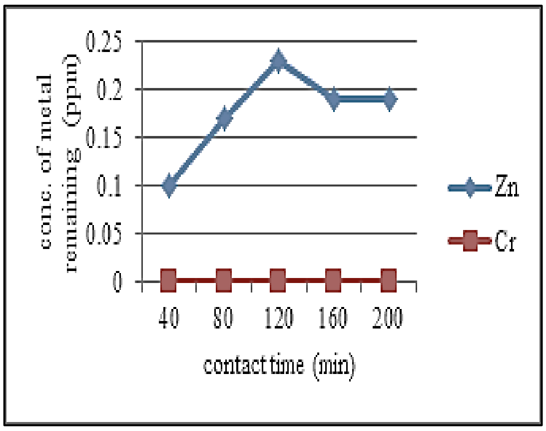

Fig. 5: *Concentration of Heavy Metal after Adsorption vs. Contact Time for Adsorbent Dosage of 5 g and 100 Micrometer Particle Size.*

From Figure 5, it is observed that the removal of Zn is maximum for the contact time of 40 min. And after 80 min, the removal is minimum and it is maybe due to the desorption of heavy metals. The Cr removal was 100% for the contact time of 40 min.

Effect of Dosage on Adsorption

Volume of waste water: 100 ml
Particle size: 100 micrometer
Contact time: 40 min (Table 4)

Table 4: *Concentration of Heavy Metal after Adsorption for Contact Time 40 mins and 100 Micrometer Particle Size.*

Sl. No	Adsorbent dosage (g)	Concentration of metal remained (ppm)	
		Zn	Cr
1	2	0.24	0
2	3.5	0.16	0
3	5	0.10	0

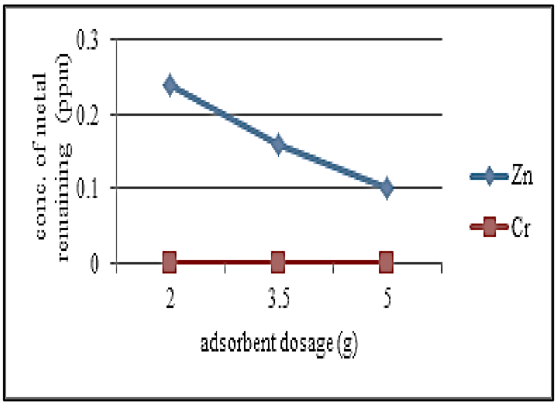

Fig. 6: *Concentration of Heavy Metal after Adsorption vs. Contact Time for Contact Time of 40 min and 100 micrometer Particle Size.*

The adsorbent dosage profile for the adsorption of chromium and zinc is shown in Figure 6. From the graph it is clear that as the adsorbent dosage increased from 2 to 5 g, the adsorption is maximum. Therefore, it is evident that as the adsorbent dosage is increased the adsorption of heavy metals can be increased.

Effect of Particle Size on Adsorption
Volume of waste water: 100 ml
Adsorbent dosage: 5 g
Contact time: 40 min (Table 5)

Table 5: *Concentration of Heavy Metal after Adsorption for Contact Time 40 min and Adsorbent Dosage 5 g.*

Sl. No	Particle size (micrometer)	Concentration of metal remained (ppm)	
		Zn	Cr
1	100	0.10	0
2	150	0.24	0
3	250	0.24	0

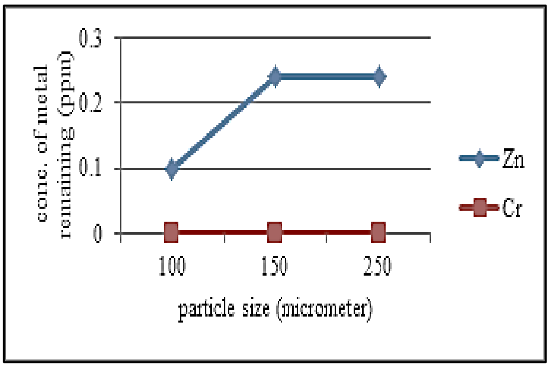

Fig. 7: *Concentration of Heavy Metal after Adsorption vs. Contact Time for Contact Time of 40 min and Adsorbent Dosage 5 g.*

From the graph in Figure 7, it is clear that as the particle size increased from 100 to 250 micron, the adsorption is minimum. Therefore, it is evident that as the particle size is decreased the adsorption of heavy metals can be increased and this is because as the particle size decreased, the surface area available for physical adsorption is increased.

Composition 2: 50% rice husk: 25% coconut shell: 25% shrimp shell
Effect of Contact Time
Volume of waste water: 100 ml
Adsorbent dosage: 5 g (Table 6)

Table 6: *Concentration of Heavy Metal after Adsorption for Adsorbent Dosage of 5 g.*

Sl. No	Contact Time (min)	Concentration of metal remained (ppm)	
		Zn	Cr
1	40	0.09	0
2	80	0.18	0
3	120	0.13	0
4	160	0.20	0
5	200	0.34	0

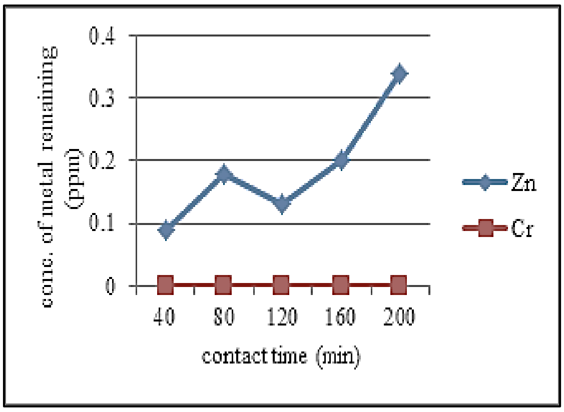

Fig. 8: *Concentration of Heavy Metal after Adsorption vs. Contact Time for Adsorbent Dosage of 5 g.*

Effect of contact time on adsorption of zinc and chromium was studied by changing the contact time at interval of 40 min keeping adsorbent dosage as 5 g. From Figure 8, it is observed that the removal of Zn is maximum for the contact time of 40 min. And after 80 min, the removal is minimum and it is maybe due to the desorption of heavy metals. The Cr removal was 100% for the contact time of 40 min.

Effect of Dosage
Volume of waste water: 100 ml
Contact time: 40 min (Table 7)

Table 7: *Concentration of Heavy Metal after Adsorption for Contact Time 40 min.*

Sl. No	Adsorbent dosage (g)	Concentration of metal remained (ppm)	
		Zn	Cr
1	2	0.21	0
2	3.5	0.07	0
3	5	0.09	0

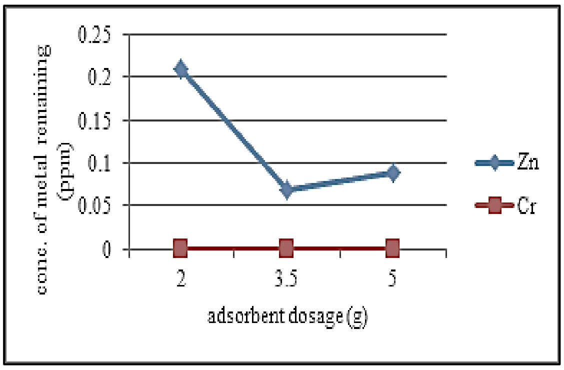

***Fig. 9:** Concentration of Heavy Metal after Adsorption vs. Contact Time for Contact Time of 40 min.*

The adsorbent dosage profile for the adsorption of chromium and zinc is shown in Figure 9. From the graph it is clear that as the adsorbent dosage increased from 2 to 3.5 g, the adsorption is increased and for 5 g the adsorption is decreased.

Composition 3: 50% coconut shell: 25% rice husk: 25% shrimp shell

Effect of Contact Time

Volume of waste water: 100 ml
Adsorbent dosage: 5 g (Table 8)

***Table 8:** Concentration of Heavy Metal after Adsorption for Adsorbent Dosage of 5 g.*

Sl. No	Contact Time (min)	Concentration of metal remained (ppm)	
		Zn	Cr
1	40	0.71	0
2	80	0.73	0
3	120	0.03	0
4	160	0.91	0

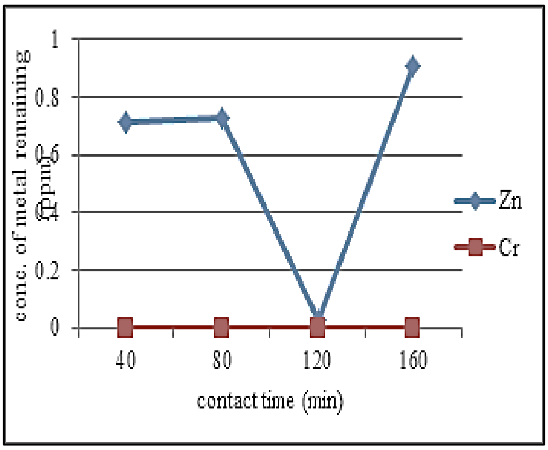

***Fig. 10:** Concentration of Heavy Metal after Adsorption vs. Contact Time for Adsorbent Dosage of 5 g.*

Effect of contact time on adsorption of zinc and chromium was studied by changing the contact time at interval of 40 min keeping adsorbent dosage as 5 g. From Figure 10, it is observed that the removal of Zn is maximum for the contact time of 120 min. The Cr removal was 100% for the contact time of 40 min.

Effect of Dosage

Volume of waste water: 100 ml
Contact time: 120 min (Table 9)

***Table 9:** Concentration of Heavy Metal after Adsorption for Contact Time 120 min.*

Sl. No	Adsorbent dosage (g)	Concentration of metal remained (ppm)	
		Zn	Cr
1	2	0.07	0
2	3.5	0.08	0
3	5	0.03	0

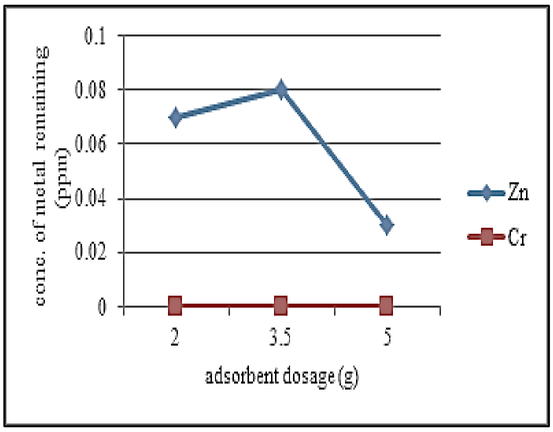

***Fig. 11:** Concentration of Heavy Metal after Adsorption vs. Contact Time for Contact Time of 120 min.*

The adsorbent dosage profile for the adsorption of chromium and zinc is shown in Figure 11. From the graph it is clear that as the adsorbent dosage increased from 2 to 5 g, the adsorption is maximum. Therefore, it is evident that as the adsorbent dosage is increased the adsorption of heavy metals can be increased.

Adsorption Isotherm

The equilibrium of adsorption is an important physico-chemical parameter for the evaluation of the adsorption process. To model the adsorption behaviour, Langmuir isotherm was studied and correlated with the experimental data, which is the earliest and simplest known relationship describing the adsorption equations [11–17].

Applicability of Langmuir Adsorption Isotherm

The data for the uptake of Zinc by the adsorbents has been determined in accordance with a linear form of Langmuir isotherm equation:

$(1/C_s) = (1/C_{max}.K_L)(1/C^*) + (1/C_{max})$ 4.5.1

The slope of the graph is represented by $1/C_{max}.K_L$, while $1/C_{max}$ shows the intercept of the graph on Y Axis. The constant C_{max} refers to the adsorption capacity and constant K_L, is an indicator for the molecular size of adsorbate. The linear line of Langmuir equation fitted well into the experimental data (Table 10).

Volume of the waste water sample taken – 100 ml

Weight of the adsorbent taken – 5 g

From the above graph in Figure 12, we get the following values:

Slope = $1/C_{max}$ K = 50

Intercept = $1/C_{max}$ = 3.81212 x 10^{-3} g/mg

Table 10: *Calculated Values for the Plotting of Adsorption Isotherm.*

Sl No.	**Initial concentration of Zn (ppm)**	**Equilibrium concentration of Zn (C*) (ppm)**	**Amount of Zn adsorbed (Cs) (mg/g)**	**1/Cs (x 10^{-3})**	**1/C* (x 10^{-4})**
1.	5246	5245.76	262.288	3.812602	1.906301
2.	5246	5245.81	262.3405	3.81183	1.90628
3.	5246	5245.75	262.2875	3.81261	1.906305
4.	5246	5245.85	262.2925	3.81246	1.90626

Cs = (Amount of Zn adsorbed/Weight of adsorbent) x Volume of solution (mg/g)   4.5.2

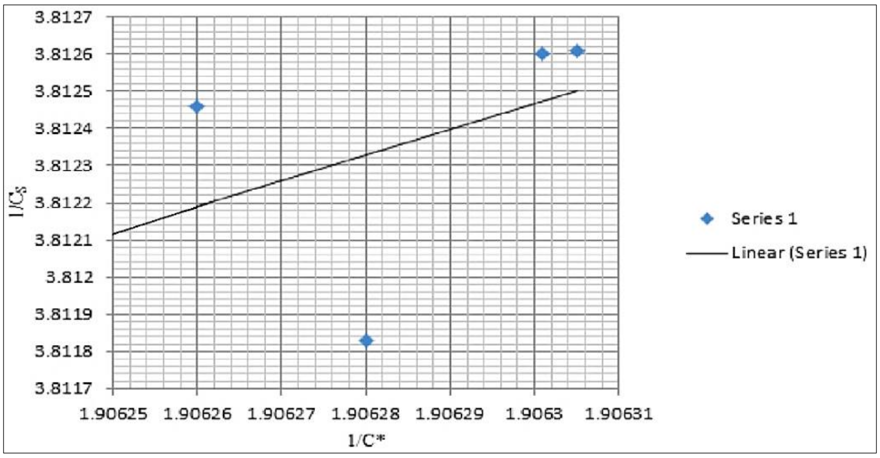

Fig. 12: *Adsorption Isotherm Plot.*

CONCLUSION

1) For adsorbent composition 1, it was seen that for contact time of 40 min, adsorption dosage of 5 g and for adsorbent particle size of 100 microns the adsorption was maximum.
2) When composition 2 was considered it was found that for dosage of 3.5 g, the adsorption was maximum and it decreased when the dosage was increased to 5 g. This decrease might have been due to desorption.
3) The amount of Zinc removed due to adsorption was maximum for composition 3 at contact time of 120 min and that for chromium was 40 min. The increase in contact time for Zinc maybe because of change in operating conditions which would have led to desorption.
4) The current adsorption study can be explained using Langmuir Isotherm.
5) In the micrometer scale, the variation in particle size had no major effect.

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