ADSORPTION OF CHROMIUM (VI) USING NEEM LEAVES AND POMEGRANATE PEELS

[1] **Raka Bhattacharjee**, [2]**Reshma Patel**
[1]M.Tech. Student, [2]Associate Professor
[1]Civil Engineering Department,
[1]BVM Engineering College, Vallabh Vidyanagar, India

Abstract— Heavy metals, when present beyond prescribed limits can be very toxic to the water in which it is dissolved. Adsorption has been used as a suitable and economical water treatment process to remove heavy metals. Many studies have been conducted to successfully remove the heavy metal by using different materials. Different materials have different chemical constituents; hence, a material that is very effective in removing one heavy metal may prove to have a poor efficiency in adsorbing, or removing, another metal. For this research, neem leaves and pomegranate peels were used as the adsorbent to remove Chromium from wastewater to compare the results of both the adsorbents. The synthetic wastewater was produced in the laboratory to conduct the experiments. Batch tests were conducted to obtain the optimal materials and conditions combinations. Different conditions are to be tested for pH 5 and adsorbent dosage. Maximum Removal with neem leaves was 65.254% and maximum Removal efficiency with pomegranate peels were 95.284%. Results have to be analyzed using Freundlich and Langmuir equations to fit the experimental data so that kinetics of the process can be obtained.

Index Terms: Neem Leaves, Pomegranate Peels, Synthetic wastewater, Adsorption

I. INTRODUCTION

All living creatures are dependent on environment. Any alterations in our environments affect adversely all the creatures living in it. Environmental pollution in recent years is one of the most challenging issues faced by humanity. It has increased exponentially in the past few decades and has reached alarming levels in terms of its effects on living creatures. All components of environment are stricken by pollution whereas water pollution is one of the serious threats to mankind.

Water is one of the environment components hit badly by pollution. With increase in industrialization and advent in technology water pollution has become a even bigger threat o the world. Among many reasons of water pollution, disposal of heavy metals is one of the cause. With increase in generation of heavy metals from technological activities, many aquatic environments face high heavy metal concentrations that often exceed water quality criteria designed to protect the environment, animals and humans. At least 20 metals are considered to be toxic, and approximately half of these metals are emitted to the environment in quantities that are hazardous to the environment, in addition to the human health. [9]

Toxic heavy metals are considered one of the pollutants as they have direct effect on man and animals. The important toxic metals i.e. Cr, Cd, Zn, Ni, Cu and Pb find its way to the water bodies through wastewaters from industries [3].Unlike most of the organic pollutants, which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products [1] and due to their non-biodegradability and persistence, can accumulate in the environment elements such as food chain, and thus may pose a significant danger to aquatic life as well as human health [7, 8]. Heavy metals can easily enter the food chain because of their high solubility in water.

The presence of heavy metal ions is of major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, oil field and refinery, textile, chloralkali, rubber, radiator manufacturing, smelting, alloy industries and storage batteries industries et. al.[2].

Water used in above industries creates wastewater that has a high potential hazard for our environment due to introduction of various contaminants such as heavy metals into soil and water resources. Heavy metal ions are among the most important pollutants found in surface and sub-surface water (Brinzo, et al., 2009). The safe and effective disposal of industrial wastewater is thus a challenging task for both industrialists and environmentalists.

Some of the treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and co-precipitation/adsorption. However some limitations of the above treatment processes are: Precipitation produces large quantities of heavy metals rich waste sludge; ion exchange and biomass methods are costly and cannot be readily applied to large scale applications [10]. Adsorption as a process is employed due to its low cost and applicability on large scales. Adsorption is commonly being done using activated carbon, which adsorbs dissolved organic substances in the water treatment [11]. Although activated carbon has its advantages, such as its effectiveness in removing colors and its applicability on wide variety of organic compounds, it has limitations that prevent it from treating highly soluble organics, and high concentrations or organic and inorganic compounds. In addition to these, its cost of operation is high. [11]

The need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research all over the world since last few decades. Low cost agricultural waste by-products such as sugarcane bagasse [23-27], Rice husk [12–16], sawdust [17–19], coconut husk [20], oil palm shell [21], neem bark [22] etc., for the elimination of heavy metals from wastewater have been investigated by various researchers. Cost is an important parameter for comparing the sorbent materials. However, cost and the expense of individual sorbents varies depending on the degree of processing required and local availability.

II. SCOPE

The scope of this thesis is to test wastewater for the removal of chromium using cheap and readily available adsorbents. The wastewater was artificially prepared in the lab. The water was tested for one adsorbent at a time, for different parameter variations in the results. The experiments were performed in the laboratory scale, and consist of batch tests. Water quality analyses of the heavy metal were done using UV- vis-spectrophotometer. The scope of this work does not include studying the chemical constituents of the adsorbents to determine the chemical reactions involved during the process. Further research into the matter is not part of the scope.

III. LITERATURE REVIEW

The most abundant metal existing in wastewater is Chromium and is considered the most dangerous metal due to it being mutagenic and carcinogenic. Adsorption is a process that collects, or adsorbs, dissolved substances in water to the surface of the materials being used as adsorbent. Adsorption has not been readily used to treat wastewater, but as the demands for better water quality become more rigorous, extensive research have been conducted on the process of adsorption to provide better quality and reduced toxicity of water.

Heavy Metal	Authors	Type of Adsorbent	Type of Test	Experimental Conditions	Results
Pb	P.Muthusamy, S. Murugan	Maize cobs, Dowex	Batch test	The initial pH values of the battery and paint effluents were 2.81 and 4.10 respectively while Pb2+concentrations were 8.96 and 9.45 mg/L respectively at 30°C.	Contact time 180minutes , 91.95%removal of Pb by dowex and 78.20% removal by maize
Cu, and Cd	A.K. Dwivedi and Dinesh Pratap Singh Rajput	Tea Factory Waste	Batch test	pH, concentrations, contact time and adsorbent dose on the adsorption was studied by uv visible spectrophotometer flask in time interval of 30, 60, 120 and 180 minuts	removal of copper and cadmium ion by tea waste is 89% and 87% respectively at optimum condition.
Fe, Pb , Cd,Cu,Ni	Hala Ahmed Hegazi	Rice husks & Fly ash	Batch Tests	Heavy metals with a concentration range of 20–60 mg/l also, using real wastewater agitation rate of 200 rpm at room temperature (25± 3). The optimum pH range for heavy metal adsorption was 6–7.0.	Percent removal using rice husk was Fe 99.25%, Pb 87.17%,Cd 67.917 %, Cu 98.177%& Ni 96.954% And using fly ash Fe 86.757%, Pb 76.06%, Cd 73.54%, Cu 98.545%,& Ni 96.034%
Cu	Kamal Rana, Mitali Shah, Nilesh Limbachiya	Sugarcane Baggase	Batch test	concentration (5, 10, 15, 20 ppm), contact time (30, 60, 90,120 min), pH (2, 3, 4, 5), adsorbent doses (0.5, 1.0, 1.5, 2 gm) at room temperature.	% removal of Cu (II) is obtained 94.4 % at pH 5, contact time 120 min, adsorbent dose of 2 gm for 5 ppm concentration.
Cr, Cu, Zn	Manal Kaakani	Palm leaves	Batch & Column Tests	PTL concentrations were 0, 2.5, 5, 7.5, and 10 g/L agitation speed of 175 rpm for two hours pHs were 3, 5, 9 initial concentrations of the metal were used were2, 6, and 10 mg/L.	Copper resulted in a maximum of 67.5% adsorption at pH 5, 99.5% chromium at pH 3, and 86% zinc at pH 9.
Cr(Vi)	Suresh Gupta, B V Babu	Neem Leaves	Batch Test	The parameters are investigated in this study included contact time, adsorbent dosage, initial Cr(VI) concentration and pH.	Activated neem leaves has a good adsorption capacity (10.4 mg/g) for the adsorption of Cr(VI)
Pb,Cd,Cu, Zn	I Nhapi, N Banadda, R Murenzi, C.B Sekomo and U.G Wali	Rice husks	Batch & Column Tests	500ml beakers at pH 7±0.2 constant temperature of 25°C	removal in batch experiment shows that the net uptake of Pb, Cd, Cu, Zn was 54.3%, 8.24%, 51.4% and 56.7%, respectively whereas using CRH, while it varied as 74.04%, 43.4%, 70.08% and 77.2% for the same dosages of ARH.

Table 2.1 Experiments done by researchers

IV. METHODOLOGY

To achieve the objective of finding an effective suitable material for adsorption of chromium, bench scale experiments were performed to obtain the effective heavy metal removal. These tests consisted of batch tests. The batch tests were conducted to determine the optimal adsorbent and operating condition to adsorb chromium metal from wastewater.

Materials

The materials that were used as the adsorbent were Neem Leaves and Pomegranate Peels. These leaves of neem tree are abundantly available locally. Although the leaves used in this research were fresh leaves, the research occurred at a small scale and it does not pose any significant effect on the environment.

After the leaves have been plugged, they have been washed thoroughly in water to remove any dust, dirt, and adhesive insoluble materials. They were then washed in distilled water to avoid having any ions from regular water contributing to variations in results. After the leaves were thoroughly washed, they were placed in the oven to dry. The temperature was set at around 105oC for around 6 hours to remove any moisture residing in the leaves. Once dried, the leaves were crushed and ground to a sieve size no larger than 0.45 mm in size. These powdered leaves which were covered and stored in a dry air-tight containers until they were used as adsorbents in the experiments.

Fresh Pomegranate Peels were collected from a nearby juice seller as a waste product. Pomegranate peels are solid wastes generated during its season from houses and juice sellers and creates a problem of municipal solid waste management. After the peels were collected they were washed thoroughly in distilled water and placed in oven at 1100C for 10 hours. After it was fully dried pomegranate peels were crushed into powder using domestic mixer and passed through sieve size of 0.45mm. These pomegranate peels were then stored in dry air tight containers to be used for experiments.

The wastewater that was used was artificially prepared in the laboratory. This was due to the fact that the effect of adsorption of metal by different adsorbent was required to be studied, as having other soluble and insoluble substances in the water would make it difficult to assess the effect of tree leaves and pomegranate on the adsorption behavior of the metal. Each adsorbent were tested individually for same optimum conditions. The water used to dissolve the metal crystals was distilled water. This was also performed to eliminate the disturbances of other soluble substances located in regular tap or drinking water. Distilled water was used to dissolve K2Cr2O7 was used to obtain chromium solution. The amount of metal crystal solids that are required to obtain an initial metal concentration of 30mg/L of solution was calculated and used in the tests. The required mass of the metal crystals to obtain these concentrations were calculated and used. The metal crystals were dissolved in 1L distilled water, and shaken until completely dissolved.

Batch Tests

Batch tests were carried out using both adsorbent individually at initial metal concentration of 30mg/l at a pH of 6 with contact time variation from 1hr, 2hr, 3 hr, 4hr, 5 hr & 6 hours and variation & adsorbent dosages variations of 1g/l, 2g/l, 3g/l, 5g/l & 10g/l with a constant agitation speed of 200 rpm and constant Temperature of $25^{o}C \pm 2$ using magnetic stirrer. The blank sample was the sample that does not contain any adsorbent. After the determined contact time when the stirring was complete, the samples were filtered to prepare for water quality analyses. Water was analyzed by Diphenylcarbazide method using UV-vis-Spectrophotometer. Once the results were obtained, they were noted to determine the percentage of metal that was removed by the different adsorbent. pH variations were done using 0.1 M H_2SO_4.

Chromium

Chromium was tested for using the AWWA 1,5-Diphenylcarbazide Standard Method 3500 Cr B and adapted from Standard Methods for the Examination of Water and Wastewater. Using UV vis Spectrophotometer a blank sample is analyzed against reference to know the absorbance at initial concentration. Then the stirred samples were analyzed one by one by adding Diphenylcarbazide solution after bringing down to pH-2 using sulphuric acid, the solution turns pinkish-purple colour depending on the concentration of the chromium in the sample, hence, the more concentrated the chromium, the more intense the colour of the solution.

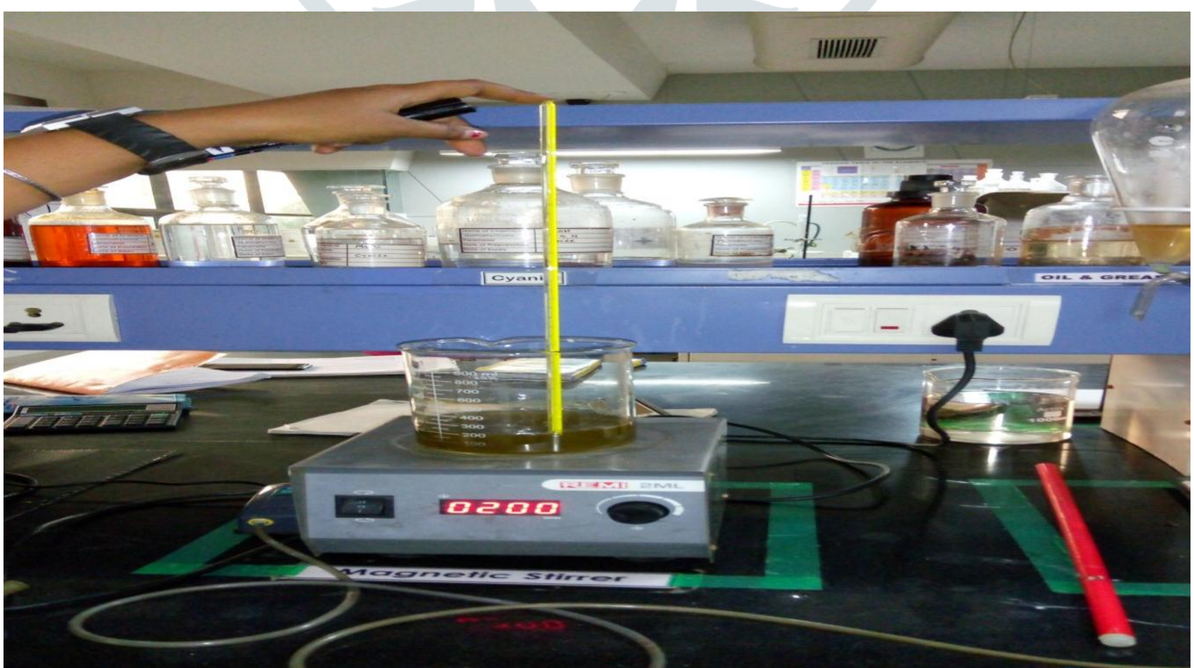

Figure 3.1 Adsorption of chromium using Neem Leaves at temperature $25^{0}C$ at stirring speed of 200 rpm.

V. RESULT & DISCUSSION

Neem Leaves

Results were analyzed by UV vis Spectrophotometer and removal percentage of metal was found by

$$\text{Removal (\%)}=[(C_o-C_e)*100]/C_o \qquad (1)$$

Where, C_o=Initial metal concentration (mg/l) before adsorption, C_e= Final Metal Concentration (mg/l) after adsorption

The results for the Neem leaves at different contact time at different dosage at pH 6 at constant temperature and stirring speed of 200 rpm are as follows using equation 1.

Contact Time(hr.)	Percentage Removal at 1g/l	Percentage Removal at 2g/l	Percentage Removal at 3g/l	Percentage Removal at 5g/l	Percentage Removal at 10g/l
1	4.537	9.313	13.045	18.478	32.328
2	8.478	14.806	16.836	25.373	39.731
3	11.642	20.299	21.791	29.403	51.313
4	16.478	24.239	24.896	37.433	63.194
5	21.552	32.657	32.567	42.866	71.433
6	22.507	33.015	39.463	47.224	68.239

Table 4.1 Removal percentage of chromium by neem leaves by adsorbent variations

Therefore the results show that the efficiency of adsorption of Neem leaves increases with adsorption dosage. The maximum removal was at 6 hours at 10g/l adsorbent dosage was 68.239% and lowest removal was at 1 hr 1g/l adsorbent dosage was 4.53%.

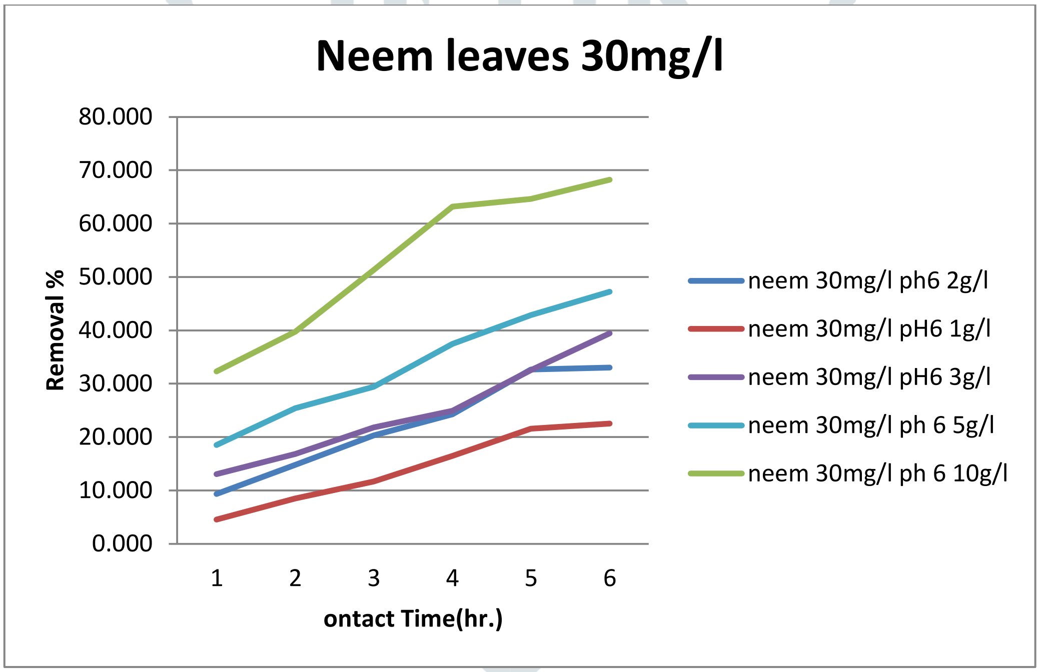

Figure 4.1 Graph showing Removal efficiencies of chromium by neem leaves

Pomegranate Peels

The results for the pomegranate peels at different contact time at different dosage at pH 6 at constant temperature and stirring speed of 200 rpm are as follows:

Contact Time(hr.)	Percentage Removal at 1g/l	Percentage Removal at 2g/l	Percentage Removal at 3g/l	Percentage Removal at 5g/l	Percentage Removal at 10g/l
1	14.209	25.343	34.119	38.269	46.657
2	20.478	31.343	37.433	41.104	52.299
3	25.194	38.119	43.851	49.104	59.761
4	30.179	44.537	50.896	55.522	68.358
5	36.836	52.746	58.806	67.104	79.015
6	45.552	66.388	77.761	88.299	95.284

Table 4.2 Removal percentage of chromium by pomegranate peels by adsorbent variations

Therefore the results show that the efficiency of adsorption of pomegranate peels increases with adsorption dosage. The maximum removal was at 6 hours at 10g/l adsorbent dosage was 95.284% and lowest removal was at 1 hr 1g/l adsorbent dosage was 14.209%.

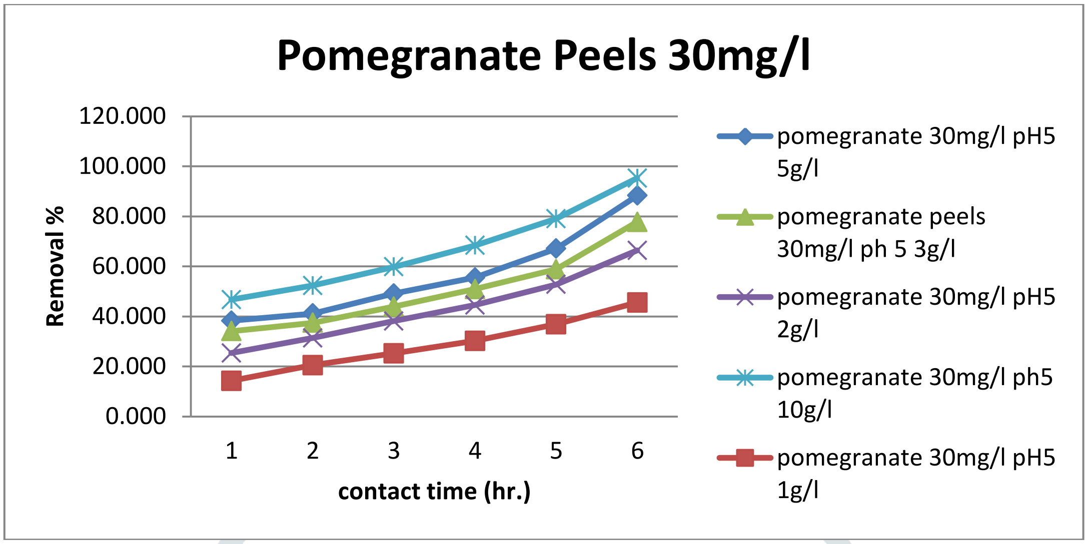

Figure 4.2 Graph showing Removal efficiencies of chromium by pomegranate peels

Adsorption Isotherms

This section presents the isotherms obtained for each adsorbent. The constants and regression coefficient are obtained. The closer the regression coefficient, R is to 1, the more accurate the points on the figure lie on the linearized isotherm line. However, if the R value is not close to 1, it does not mean that the experiments are unreliable; rather, it refers to the inability of the points to be linearized using the mentioned isotherm. Langmuir and Freundlich were used due to their widespread application in adsorption.

The capacity of the adsorbents determines the amount of heavy metal that was adsorbed onto the adsorbent, and can be determined through the following mass balance equation

$q_e = (C_o - C_e)V/m$ (2)

q_e represents the adsorbent concentration after equilibrium (mg absorbent/g absorbent), V represents the total volume of the solute solution (in L), Co represents the initial concentration of the solute (in mg/L), C_e the residual equilibrium concentration of the solute after adsorption (in mg/L), and, m represents the weight of the adsorbents used (in g)

For Neem Leaves

C0 (mg/l)	Ce1 (mg/l)	Ce2 (mg/l)	Ce(avg) (mg/l)	C0-Ce (mg/l)	qe (mg/g)	Ce/qe	Dosage (g/l)	log(x/m)	log Ce
30	10.890	8.167	9.528	20.472	2.047	4.654	10	0.311	0.979
30	16.890	14.776	15.833	14.167	2.833	5.588	5	0.452	1.200
30	18.054	18.269	18.161	11.839	3.946	4.602	3	0.596	1.259
30	20.149	18.358	19.254	10.746	5.373	3.583	2	0.730	1.285
30	23.248	22.460	22.854	7.146	7.146	3.198	1	0.854	1.359

Table 4.3 Isotherm Models for Chromium (VI) using Neem Leaves at pH 6 and initial concentration of Cr^{6+}

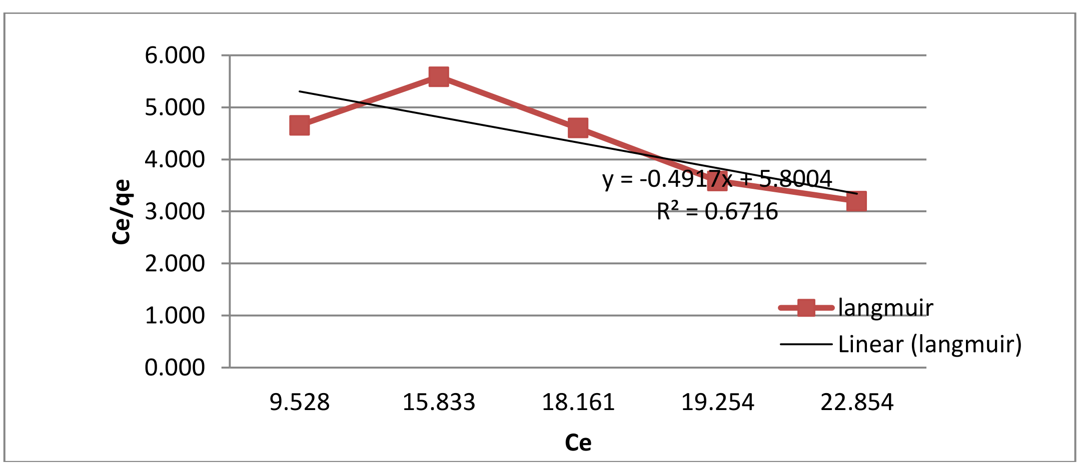

Figure 4.3: Langmuir Isotherm for Chromium at 30 mg/L Co and at pH 6 with Neem leaves

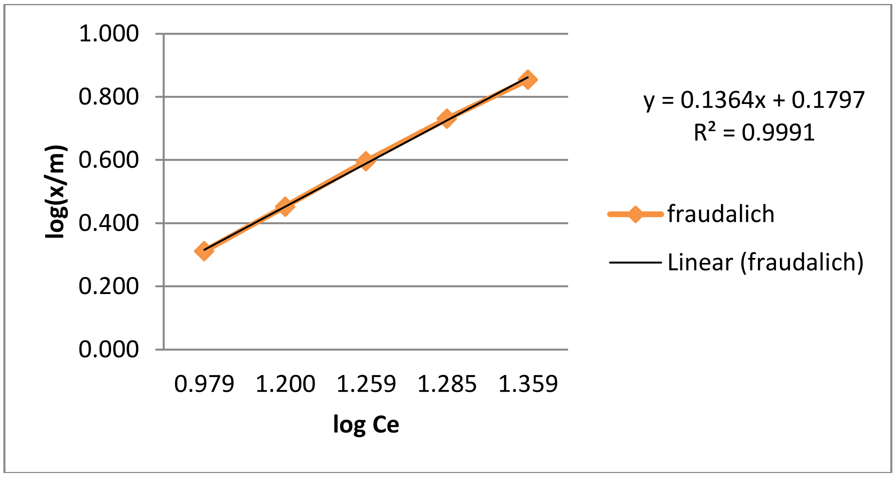

Figure 4.4: Freundlich Isotherm for Chromium at 30 mg/L Co at pH 6 with Neem leaves

Results revealed that Freundlich adsorption isotherm was the best model for the metal ions adsorption onto Neem leaves with of R^2=0.999.

For Pomegranate Peels

C0(mg/l)	Ce1(mg/l)	Ce2(mg/l)	Ce (avg) (mg/l)	C0-Ce (mg/l)	qe (mg/g)	Ce/qe	Dosage (g/l)	log(x/m)	log Ce
30	16.155	15.851	16.003	13.997	13.997	1.143	1	1.146	1.204
30	10.496	9.672	10.084	19.916	9.958	1.013	2	0.998	1.004
30	6.197	7.146	6.672	23.328	7.776	0.858	3	0.891	0.824
30	3.475	3.546	3.510	26.490	5.298	0.663	5	0.724	0.545
30	1.684	1.146	1.415	28.585	2.859	0.495	10	0.456	0.151

Table 4.4 Isotherm Models for Chromium (VI) using Pomegranate Peels at pH 6 and initial concentration of Cr^{6+}

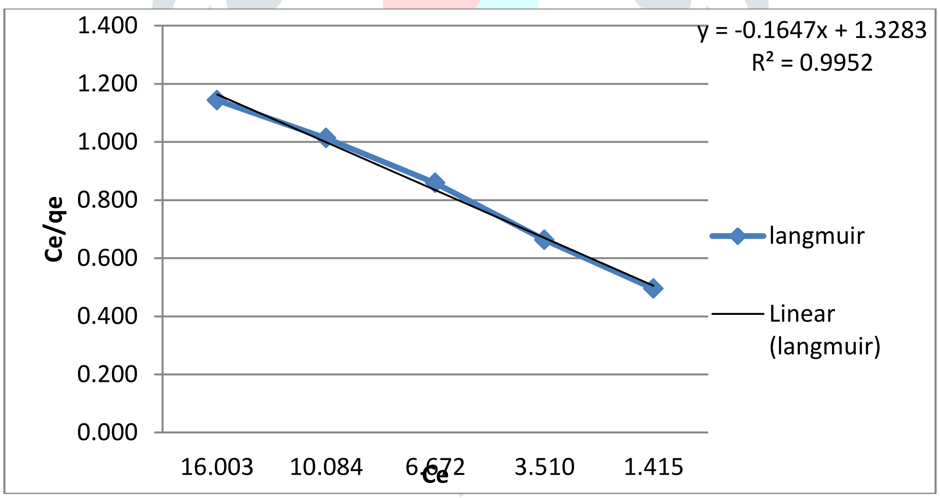

Figure 4.5: Langmuir Isotherm for Chromium at 30 mg/L Co and at pH 6 with pomegranate peels

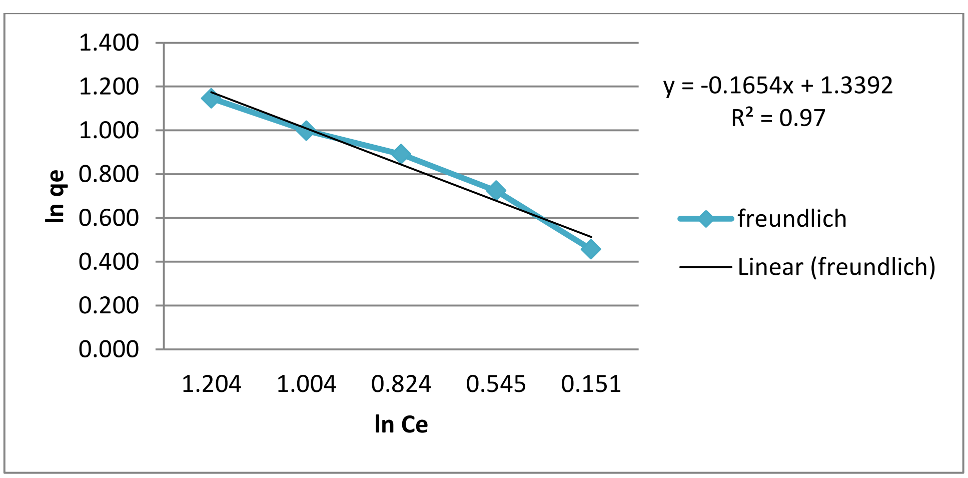

Figure 4.6: Freundlich Isotherm for Chromium at 30 mg/L Co at pH 6 with pomegranate peels

Results revealed that both Freundlich as well as Langmuir adsorption isotherm fitted nicely for the metal ions adsorption onto pomegranate peels.

VI. CONCLUSION

From the results it can be concluded that efficiency of Pomegranate Peels was more compared to neem leaves at pH 6 at initial metal concentration 30mg/l. Langmuir and Freundlich adsorption isotherms were used to linearize the data obtained from the batch tests. For neem leaves freundlich isotherm fitted best but for pomegrate peels both Lagmuir isotherm and Freundlich isotherm fit nicely.

REFERENCES

[1] Ajmal, M., A. Mohammad, R. Yousuf and A. Ahmad,1998. Adsorption behavior of Cadmium, Zink, Nickel, and Lead from aqueous solution by Mangifera India Seed Shell. India J. Environ Hlth. 40: 15-26.

[2] Azza Khaled, Ola Abdelwahab, Amany El-Sikaily Ahmed El Nemr, "Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed," Journal of Hazardous Materials, vol. 152, pp. 263-275, 2008.

[3] Bakkaloglu, I., T.J. Butter, L.M. Evison, F.S. Holland and I.C. Hancock, 1998. Screening of various types biomass for removal and recovery of heavy metals (Zn,Cu, Ni) by biosorption, sedimentation and desorption. Sci. Tech., 38: 269-277

[4] Bansal, O.P., 1996. Heavy metal pollution of soils and plants to sewage irrigation. India J. Environ Hlth., 40:51-57.

[5] D. Mohan, K.P. Singh, Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse – an agricultural waste, Water Res. 36 (2002) 2304–2318.

[6] E. Munaf, R. Zein, The use of rice husk for removal of toxic metals from wastewater, Environ. Technol. 18 (1970) 359–362.

[7] J.P. Pope, "Activated Carbon and some applications for the remediation of soil and groundwater pollution," Virginia Tech, Virginia, 1996.

[8] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Bioresour. Technol. 76 (2001) 63–65.

[9] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solution, Bioresour. Technol. 87 (2003) 129–132.

[10] K. Selvi, S. Pattabhi, K. Kadirvelu, Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon, Bioresour. Technol. 80 (2001) 87–89.

[11] K. Srinivasan, N. Balasubramaniam, T.V. Ramakrishna,Studies on chromium removal by rice husk carbon, Indian J.Environ. Health 30 (4) (1998) 376–387.

[12] Kaewsarn, P. and Q. Yu, 2001. Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga Padina sp. Environmental Pollution, 112: 209-213

[13] M. Ajmal, R.A.K. Rao, B.A. Siddiqui, Studies on removal and recovery of Cr (VI) from electroplating wastes, Water Res. 30 (6) (1996) 1478–1482.

[14] M. Ajmal, R.A.K. Rao, S. Anwar, J. Ahmad, R. Ahmad,Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater, Bioresour. Technol. 86 (2003) 147–149.

[15] Metcalf & Eddy, Wastewater Engineering, Treatment and Reuse. New York, USA: McGraw-Hill, 2004.

[16] N.A. Khan, M.G. Shaaban, MH.A. Hassan, Removal of heavy metal using an inexpensive adsorbent, in: Proc. UM Research Seminar organized by Institute of Research Management and Consultancy (IPPP), University of Malaya, Kuala Lumpur, 2003.

[17] N.A. Khan, M.G. Shaaban, Z. Jamil, Chromium removal from wastewater through adsorption process, in: Proc. UM Research Seminar 2003 organized by Institute of Research Management and Consultancy (IPPP), University of Malaya, Kuala Lumpur, 2003

[18] N.A. Khan, S.I. Ali, S. Ayub, Effect of pH on the removal of chromium (Cr) (VI) by sugar cane baggase, Sci. Technol. 6(2001) 13–19.

[19] R. Suemitsu, R. Venishi, I. Akashi, M. Nakano, The use of dyestuff-treated rice hulls for removal of heavy metals from waste water, J. Appl. Polym. Sci. 31 (1986) 75–83.

[20] S. Ayub, S.I. Ali, N.A. Khan, Adsorption studies on the low cost adsorbent for the removal of Cr(VI) from electroplating wastewater, Environ. Pollut. Control J. 5 (6) (2002) 10–20.

[21] S. Ayub, S.I. Ali, N.A. Khan, Efficiency evaluation of neem (Azadirachta indica) bark in treatment of industrial wastewater,Environ. Pollut. Control J. 4 (4) (2001) 34–38.

[22] S. Ayub, S.I. Ali, N.A. Khan, R.A.K. Rao, Treatment of wastewater by agricultural waste, Environ. Prot. Control J. 2 (1)(1998) 5–8.

[23] S. Ayub, S.I. Ali, N.A. Khan, Study on the removal of Cr(VI) by sugarcane bagasse from wastewater, Pollut. Res. J. 2 (2) (2001)233–237.

[24] V.K. Gupta, M. Gupta, S. Sharma, Process development for the removal of lead and chromium from aqueous solution using red mud – an aluminum industry waste, Water Res. 35 (5) (2001) 1125–1134.

[25] W.T. Tan, S.T. Ooi, C.K. Lee, Removal of chromium (VI) from solution by coconut husk and palm pressed fibre, Environ. Technol. 14 (1993) 277–282.

[26] Yan, G. and T. Viraraghavan, 2001. Heavy metal removal in a biosorption column by immobilized M.rouxii biomass. Bioresource Technology, 78: 243- 249

[27] Yetis, U., G. Ozcengiz, B. Filiz, N. Ergen, A. Erbay and A. Dolek, 1998. Heavy Metal biosorption by White-Rot Fungi. Wat. Sci. Tech., 38: 323-330.