

Utilization of Activated Carbon for the Removal of Ni Metal from Industrial Liquid Waste

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ABSTRACT

Environmental pollution caused by toxic metals seems to occur globally. Metal intoxicated wastewater can be challenging to health safety. The high concentration of pollutants is required to be removed before the discharge of wastewater into open waste streams. The present study relates the monitoring of heavy metals in the industrial waste coming from Shairshah, Lyari SITE industrial area and control sites selected from Clifton beach of Karachi (Pakistan). Concentrations of selected trace metals, Cr, Fe, Hg, Na, K, Cd, Pb, Ni, Zn, Mo, Mn and Cu were estimated by using Atomic Absorption Spectrophotometer, Flame Photometer and 200 Multi parameter Ion Specific Meter under standard analytical conditions. Statistical methods of relevance were applied to check the accuracy of the system. Selective removal of Ni metal from waste water was carried out by adsorption process using activated carbon prepared from agricultural waste. The effectiveness of the adsorption process has been tested under the optimized conditions of temperature, concentration, stay time and amount of adsorbent. Adsorption isotherm models like Freundlich and Langmuir were applied to determine the feasibility of process by finding the values of their respective constants. The R^2 values show that Langmuir model was the best fitted adsorption model. The feasibility of adsorption process was determined by R_L factor. Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the system were calculated. The sorption free energy (E_s) was also estimated. The pH_{pzc} of adsorbent was also estimated by adopting pH drift method. The percentage removal and distribution coefficient (K_D) values for Ni removal were also determined. The present system represents that Ni and other metals can be effectively removed by employing adsorption method using low cost natural adsorbents.

Keywords: Industrial waste, Ni metal removal, adsorption isotherms, pH_{pzc}

1. INTRODUCTION

In most developing countries of the world, environmental pollution stems generally from weak economy, low priorities for hygienically sound living, high illiteracy, mismanagement and unrealistic planning. Pakistan is no exception to this situation. Infact, the environmental problems of the country are manifold, namely, water, air, noise, solid and hazardous waste pollution arises from various industries due to mismanagement, rapid urbanization, deforestation, erosion, sedimentation, water logging and salinity etc, which have reached to an alarming status¹. Only 79% urban and 44% rural population has access to treated water supply. The rest consumes untreated ground water from shallow ground aquifers, which are occasionally contaminated with industrial effluents and sewage. Only 40% of country's populations discharge their sewage into sewer lines. This may also pave its way to agricultural fields and utilized untreated. Indiscriminate and continuous disposal of untreated industrial effluents into waterways damages the aquatic eco system².

Karachi, being the largest city of Pakistan, has been facing the acute environmental problems since it's vast spreading development, rapid urbanization and industrialization, unsatisfactory sewage system, untrained workers, lack of resources of utilization and distribution systems of municipal corporation, the chances of contamination of drinking water with the sewage system has been enormous³.

Awareness of water pollution is increasing day by day. Due to rapid urbanization and industrialization, the natural biology of the environment has severely been disturbed. Among the various sources of pollutants in surface and ground water, atmospheric emissions from industry, households and run-off from agricultural fields have contributed to water pollution. It is estimated that industrial and domestic waste water introduces a very large number of different pollutants into natural water, such as polycyclic aromatic compounds, pesticides, radio active matters and trace metals. The latter group of pollutants which is especially dangerous for human health is trace metals⁴.

Changing climatic conditions affect on discharge rates, as well as residence time of trace metals. Different environmental conditions in estuarine systems can affect trace metal speciation, removal rates, and thus fluxes of trace metals that reaches the ocean⁵⁻⁸.

Many industrial manufacturing processes produce wastewater containing heavy metals. As a result of improper treatment prior to discharge, many dissolved metals have been found in harmful concentrations in groundwater which are destined for potable drinking water. In small quantities, certain heavy metals are nutritionally essential for healthy life, but excess amounts of any of them may cause acute or chronic toxicity. Most of the metals are required by human in trace amounts, but in larger and persistent dosages, these heavy metals become toxic when they are not metabolized by the body and accumulate in soft tissues. Heavy metal toxicity can result in damaged or reduced mental and central nervous system functions, lower energy levels, and damages to blood composition, lungs, kidneys, liver, and other vital organs⁹.

There are different types of water pollution among these are acid drainage, thermal pollution, effluents from petroleum refining and oil spills, radioactive materials. Small quantity of variety of metals are released by almost every industry since many of these are toxic and relatively little is known about their cycling in the biosphere, they constitute a real problem¹⁰.

Different methods were employed for the purification of waste like biological treatments, membrane processes, advanced oxidation processes, electrochemical techniques and adsorption procedures¹¹. These are widely used for removing metals and organic compounds from industrial effluents. Amongst all the proposed treatment methods adsorption using sorbents is one of the most popular method it produces high-quality treated effluents. Adsorption is a well-known equilibrium separation technique. It is now recognized as an effective, efficient and the most economic method for the water decontamination applications and analytical separation purposes. The adsorbents may be of mineral, organic or biological origin like activated carbons, zeolites, clays, and silica beads¹².

Recently, numerous approaches have been studied for the development of low cost natural and modified adsorbents. In the present studies, sugarcane baggase has been utilized for the preparation of activated carbon as a replacement for current conventional methods of removing pollutants from industrial waste.

2. EXPERIMENTAL METHODS

2.1 Sample collection

Industrial liquid waste samples were collected from the Shershah and Lyari industrial area of Karachi city while control samples were collected from Clifton beach. The details of sampling sites (ML₁ to ML₈) are presented in Fig.1

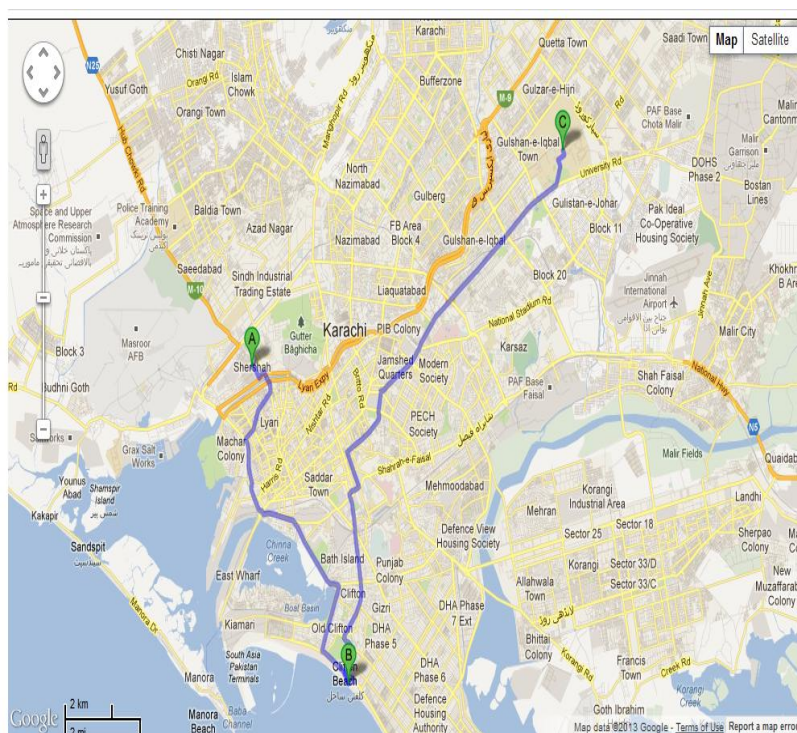


Fig-1: Location map of sampling sites (A. Shershah, Lyari site B. Clifton beach)

2.2 Samples preservation

Samples were collected in pre cleaned plastic bottles. Each sample bottle was labeled so that contents would be identified separately. The samples were stored by adding 10 ml of nitric acid (65%) in each flask and keep them at cool place.

2.3 Digestion of liquid waste samples

The liquid waste samples were digested with nitric acid (65%) by adopting wet oxidation method. 100 ml of the liquid waste sample was added in 50 ml nitric acid. The content was heated at 60 ± 2 °C until one third portion of the sample was left behind. The digested samples were filtered and transferred to 100 ml volumetric flask and solution was made up to the mark with deionized water.

2.4 Sample Analysis

Digested liquid waste samples were analyzed by Atomic Absorption Spectrophotometer (AA-2380) for the measurements of metal concentrations: Cr, Mo, Cu, Mn, Zn, Pb, Hg, Co, Ni, Fe and, Cd. While Na and K were

analyzed by flame photometer and Hg was analyzed by cold vapor atomic absorption technique¹³. Triplicate samples were run in order to ascertain the precision of data.

2.5 Removal of Ni metal from liquid waste

The removal of excess concentration of metal was carried out by adsorption method. The Ni was found to have higher concentration in sample MLO₁ compared to other metals, so it was selected for the removal studies by using activated carbon. The activated carbon was prepared by carbonization of agricultural waste at 1000 °C by keeping in muffle furnace.

3. BATCH ADSORPTION STUDIES

The adsorption experiments were run under the optimized conditions of amount of adsorbent, stay time and concentrations at temperatures ranges from 30 to 45°C.

3.1 Optimization of amount of adsorbent

For the optimization of amount of activated carbon, 50 ml of 100 ppm of Ni standard solution was taken in shaking flasks by adding 0.1, 0.2, 0.3, 0.5 and 1.0 gm of activated carbon. The content was shaken for 30 minutes at 30°C. After the specific time period the contents were filtered and concentration of metals were analyzed by atomic absorption spectrophotometer¹⁴⁻¹⁶.

3.2 Optimization of stay time

For the optimization of stay time 50 ml of 100 ppm Ni solution was added in shaking flask for the variable time period from 5 to 60 minutes at 30°C. After specific time period each flask was filtered and analyzed by Atomic Absorption Spectrophotometer¹⁶.

3.3 Adsorption Experiments

Adsorption experiments were run at 30 to 45°C. The solution concentrations were varied from 20 to 60 ppm by keeping the optimum amount of adsorbent and shaking time.

4. RESULTS AND DISCUSSION

4.1 Concentration of trace metals in industrial liquid waste samples

The digested industrial liquid waste samples (ML₁ to ML₈, MLO₁, MLO₂ and control water sample) were analyzed by atomic absorption spectrophotometer. Concentrations of trace metals Mo, Cr, Cu, Mn, Zn, Pb, Hg, Co, Ni, Fe, Cd, Na and K in liquid waste samples were determined as shown in Table-1 and Fig-2. The results show that Cr metal was found to be (0.096 mg/L) concentration in sample ML₃. The concentrations of Mo, Cu, Fe and Pb metals were high in MLO₁ and ML₄ samples, which were collected from site industrial area of Karachi city and Clifton beach as control site. The higher levels of Mn and Zn metals were 1.880 mg/L and 43.5 mg/L respectively were found in MLO₂ sample. The Hg was shown in sample number ML₃ about 0.018 mg/L, whereas the reported permissible level in NEQS is 0.01 mg/L. The concentration of Co 30.07 mg/L was found in ML₂ sample which was collected from Layri site. Ni metal in sample MLO1 shows the 260.0 mg/L, which was the highest concentration compare to other respective sample. The Cd was 0.050 mg/L was found in sample ML₅.

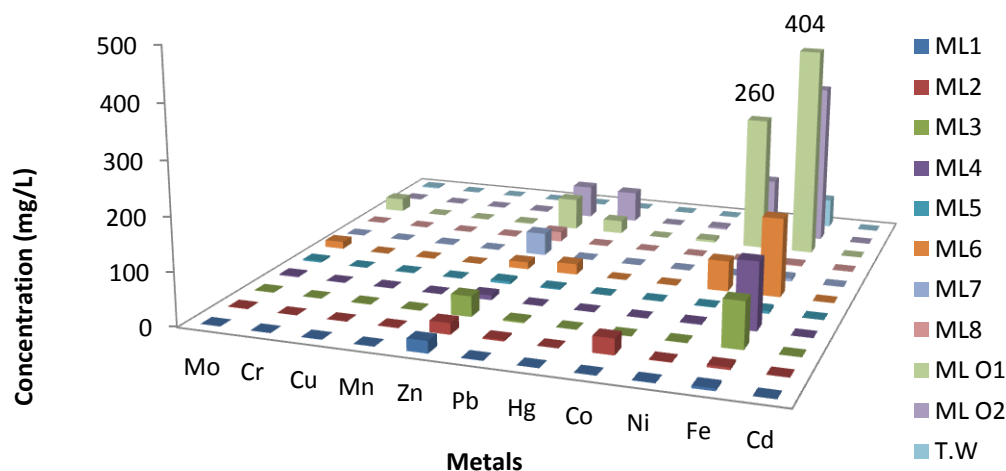


Fig-2: Concentration of trace metals (mg/L) in the industrial liquid waste samples

Table-1: Concentration of heavy metals (mg/L) in industrial waste sample

S. No	Sample	Mo	Cr	Cu	Mn	Zn	Pb	Hg
1	ML1	0.26	0.042	0.75	0.20	22.5	0.57	0.014
2	ML2	1.16	0.026	0.40	0.70	21.25	2.58	0.013
3	ML3	0.90	0.096	0.80	0.56	38.4	2.69	0.018
4	ML4	2.30	0.013	0.98	0.53	9.00	0.13	0.011
5	ML5	3.03	0.023	0.55	0.60	5.00	2.23	0.014
6	ML6	14.0	0.007	0.93	0.23	13.6	20.5	0.001
7	ML7	0.13	0.07	0.93	0.30	43.5	0.71	0.003
8	ML8	0.06	0.049	0.14	1.18	19.5	1.03	0.003
9	ML O1	26.0	0.016	0.57	1.57	61.5	25.5	0.002
10	ML O2	0.86	0.017	0.72	1.88	63.5	60.0	0.001
11	Control	2.40	0.009	0.10	0.20	0.59	0.19	BD

S. No	Sample	Co	Ni	Fe	Cd	Na	K
1	ML1	0.05	0.78	4.60	0.04	1907.3	38.89
2	ML2	30.0	1.16	4.61	0.041	2459.4	50.22
3	ML3	0.05	0.71	87.0	0.04	451.73	42.29
4	ML4	0.06	1.76	127	0.039	833.2	46.06
5	ML5	0.14	0.42	5.24	0.05	4700	679.7
6	ML6	0.39	58.0	149.7	0.048	9034.7	566.4
7	ML7	0.02	0.42	5.61	0.039	15052.7	17.74
8	ML8	0.02	0.18	1.81	0.039	1221.36	47.95
9	ML O1	4.40	260	404	0.049	8532.85	566.4
10	ML O2	3.20	112	310	0.049	1208.2	346.1
11	Control	0.04	0.04	56.0	0.04	59.00	15.00

Key for abbreviations: ML= Mix liquid, MLO= Mix liquid oil, T.W= Tap water. BD: Below detection limit

4.2 Statistical treatment of data

Table 2 and 3 show the statistical parameters and correlation coefficient (r^2) values. The strong positive correlation 0.95 was found in Cd-K.

Table-2: Statistical parameters of analyzed metals

S.NO	METALS	Range	Average	\pm SD	Median
1	Cr	0.007- 0.069	0.033	0.028	0.02
2	Mo	0.060 – 26.00	4.645	8.110	1.16
3	Cu	0.100 - 0.980	0.631	0.312	0.72
4	Mn	0.200 -1.880	0.725	0.574	0.56
5	Zn	0.590 - 63.50	27.12	21.60	21.2
6	Pb	0.130 - 60.0	10.55	18.61	2.23
7	Hg	0.001 - 0.018	0.007	0.006	0.003
8	Co	0.020 - 30.07	3.745	8.877	0.140
9	Ni	0.040 - 260	39.58	81.40	0.780
10	Fe	404 - 0.56	100.0	139.8	5.610
11	Cd	0.39 - 0.050	0.040	0.004	0.040
12	Na	451.73 - 15052	4540	4836	1229
13	K	17.748 - 3346	540.2	1021	49.00

Table-3: Metal to metal correlation in industrial waste samples

Metals	Cr	Mo	Cu	Mn	Zn	Pb	Hg	Co	Ni	Fe	Cd	Na	K
Cr	1												
Mo	-0.39	1											
Cu	0.22	0.07	1										
Mn	-0.14	0.29	-0.17	1									
Zn	0.27	0.32	0.27	0.71	1								
Pb	-0.33	0.31	0.16	0.74	0.67	1							
Hg	0.43	-0.38	0.26	-0.29	-0.02	-0.43	1						
Co	-0.14	-0.02	-0.24	0.12	0.042	-0.01	0.21	1					
Ni	0.33	0.85	0.04	0.68	0.68	0.65	-0.04	0.005	1				
Fe	-0.32	0.71	0.25	0.72	0.71	0.79	-0.03	-0.06	0.92	1			
Cd	-0.50	0.58	0.09	0.47	0.30	0.67	-0.02	-0.03	0.63	0.62	1		
Na	0.08	0.41	0.38	0.01	0.29	0.002	-0.03	-0.01	0.26	0.10	0.20	1	
K	-0.48	0.65	0.12	0.31	0.14	0.469	-0.18	-0.12	0.57	0.52	0.95	0.32	1

4.3 Adsorption studies

The adsorption experiments were preceded under the optimized amount of activated carbon and stay time for the removal of Ni metal as shown in Fig 3 and 4. The adsorption isotherms were drawn by varying the temperatures (30 - 45 °C) for the removal of Ni metal.

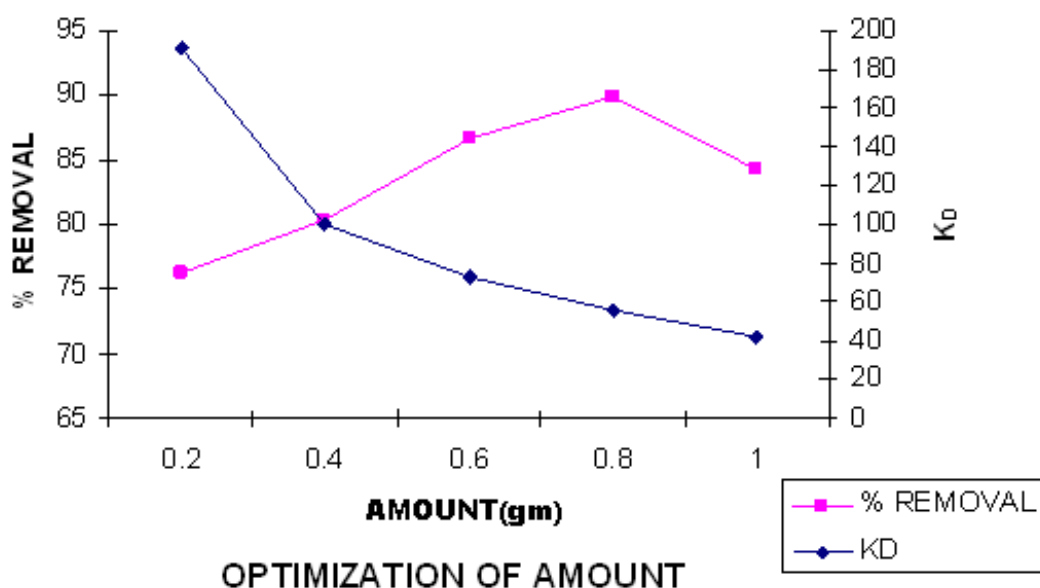


Fig-3: Optimization of amount of activated carbon for the removal of Ni

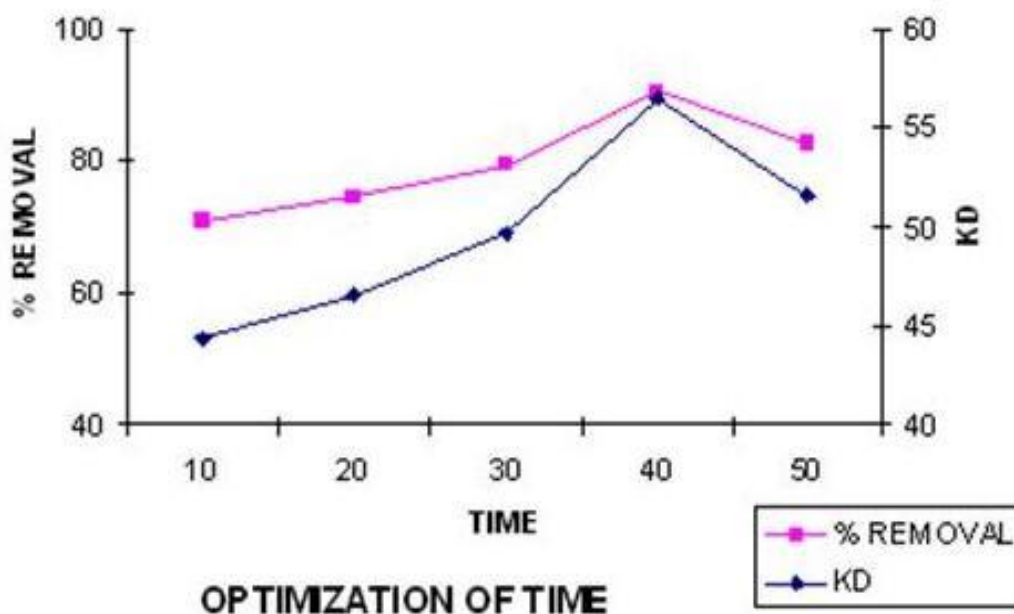


Fig-4: Optimization of time of activated carbon for the removal of Ni

4.4 Effect of adsorbent dose

To determine the effect of adsorbent dose, different amounts (0.1 to 1.0 gm) of adsorbent were suspended in 50 ml Ni standard solution having concentration 100 ppm under the optimized amount and stay time (Allen *et al.*, 2000). The effects of adsorbent dose on the amount of nickel adsorbed (in mg/g) are shown in Fig. 3. The results show that amount of adsorbent significantly influenced the extent of nickel adsorption.

4.5 Effect of contact time

Fig.4 shows the comparative data of the effect of contact time on the extent of adsorption of Ni on the activated carbon at 100 ppm keeping the temperature 303 K. It has been observed that the metal adsorption rate is high in the beginning and then decreases slowly till saturation levels were completely reached at the equilibration point.

5. ADSORPTION ISOTHERM MODELING

Adsorption isotherm is a graphical representation between the bulk activity of adsorbate and amount adsorbed at constant temperature. It characterized the distribution of adsorbed solute between the adsorbate and solid phases at various equilibrium concentrations.

The effect of temperature on the removal tendency of dye was also studied at temperatures ranges from 303 – 318 K. The critical review of adsorption isotherm shows a decrease in the adsorption of dye with the rise in temperature, which signifies the adsorption of metal on activated carbon is temperature dependent in nature.

5.1 Freundlich Adsorption Isotherm

Freundlich expressed an empirical equation for representing the isothermal variation of adsorption on the quantity of gas adsorbed by unit mass of solid adsorbent with concentration. It is expressed as;

$$\text{Log } X/m = \text{Log } K + 1/n \text{ Log } C_e \text{ ----- (1)}$$

Where X/m is the amount adsorbed per unit mass of the adsorbent (mol/g), C_e is the equilibrium concentration (mol/dm³) and the constant K relates to the degree of adsorption, while n provides the rough estimation of the intensity of the adsorption process¹⁷. Freundlich plot was obtained at various temperatures 303 – 318 K, as shown in Fig 5. The decrease in the values of K with the rise in temperature indicates the adsorption affinity of metal on activated carbon is less favorable at higher temperatures but its value change randomly. The values of respective constants K and n are shown in Table-4.

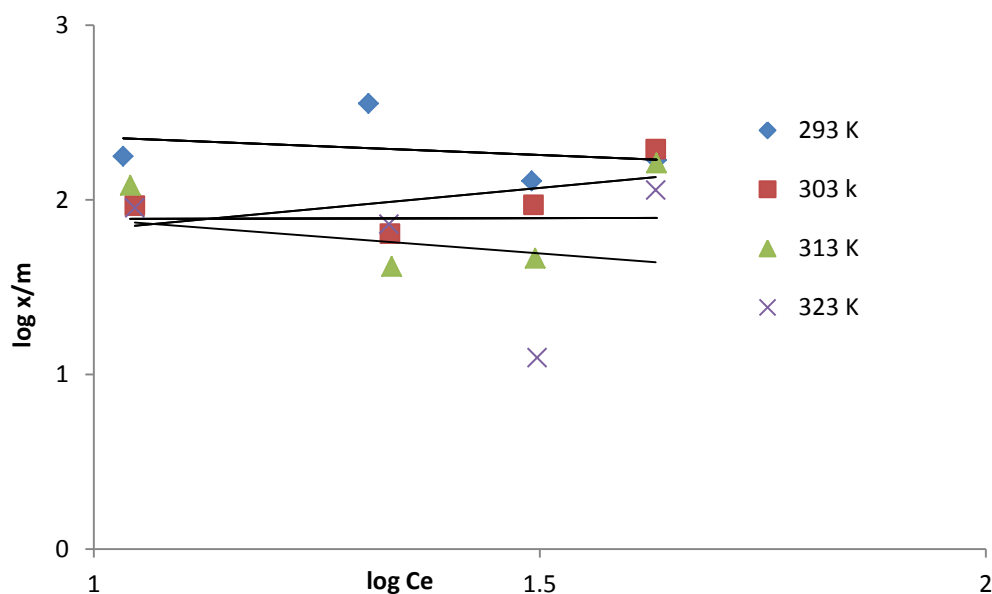


Fig-5: Freundlich isotherm for the removal of Ni by activated carbon

Table-4: Freundlich parameters for the removal of Ni

S.No	Temperature (K)	K	n	Intercept	Slope	R ²
1.	293	363.078	-4.90	2.56	-0.20	0.080
2.	303	22.387	2.13	1.35	0.47	0.350
3.	313	75.857	125.0	1.88	0.01	0.005
4.	323	190.546	2.57	2.28	0.39	0.050

5.2 Langmuir Adsorption Isotherm

The Langmuir isotherm assumes monolayer adsorption on homogeneous surfaces with a finite number of adsorption sites. The linear equation is expressed as:

$$C_e/X/m = 1/kV_m + C_e/V_m \text{ ----- (2)}$$

Where C_e is the equilibrium concentration of adsorbate in (mol/dm³), X/m is the amount adsorbed at equilibrium (mol/g) and V_m (mol/g) and k (dm³/mol) is Langmuir constants related to monolayer capacity and adsorption coefficient respectively¹⁸. The linear plot of $C_e/X/m$ vs. C_e is shown in Figure 6. The value of monolayer capacity V_m and Langmuir constant k were determined from intercept and slopes of the respective plot are represented in Table 5.

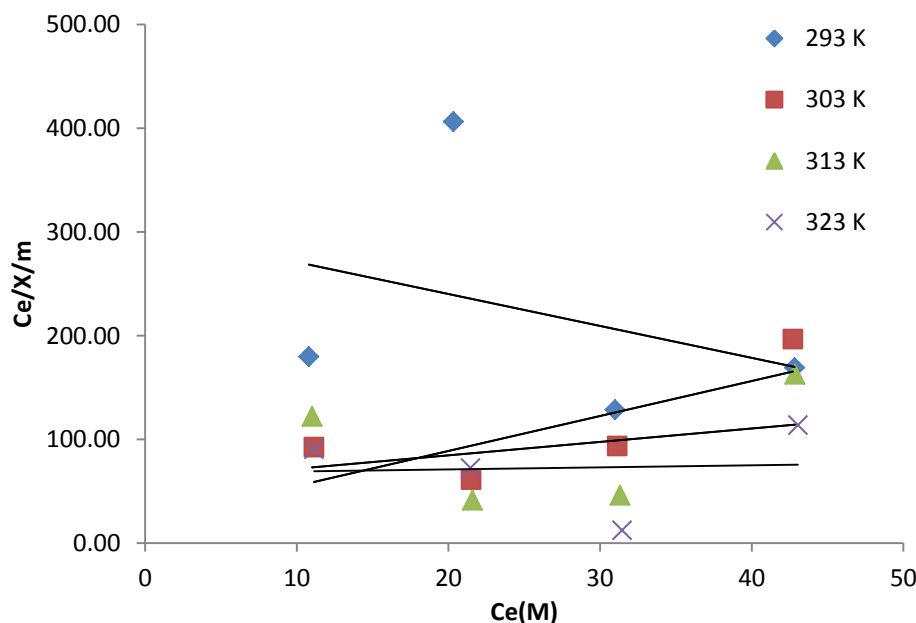
The essential characteristics of the Langmuir isotherm is that it is a dimensionless constant which relates to separation factor or equilibrium parameter R_L as given by,

$$R_L = 1/1+kC_i \quad \text{----- (3)}$$

Table-5: Langmuir parameters for the removal of Ni

S.No	Temperature (K)	K	V _m	Intercept	Slope	R ²
1.	293	0.01	-0.32	301.70	-3.08	0.11
2.	303	0.16	0.30	21.38	3.37	0.59
3.	313	0.02	0.77	58.72	1.29	0.09
4.	323	0.00	5.08	67.08	0.20	0.00

Where k represents the Langmuir constant and C_i is the initial concentration (mol/dm^3). The parameter R_L shows whether the adsorption system is favorable if ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$)¹⁹.

**Fig-6:** Langmuir isotherm for the removal of Ni by activated carbon

5.3 pH_{pzc}

The surface functional groups and pH_{pzc} are important characteristics for any adsorbent as they indicate the acidity/basicity of the adsorbent, type of adsorbent (either H- or L-type), and the net surface charge of the adsorbent (carbon) in solution. The combined influence of all the functional groups of activated carbon determines pH_{pzc} , i.e., the pH at which the net surface charge on carbon was zero. At $pH < pH_{pzc}$, the carbon surface has a net positive charge, while at $pH > pH_{pzc}$ the surface has a net negative charge²⁰.

For the investigation of point zero charge of carbon, the values of final versus initial pH were plotted as shown in Fig 7 at 24 and 48 hours time interval. From the graph, the values of $pH_{(pzc)}$ of charcoal were determined from the points where the initial pH was equal to the final pH. As shown in the Table 6, the pH values indicate that the surface of charcoal was acidic in nature since the $pH_{(pzc)}$ values were transformed from acidic to basic and then eventually reached to acidic representing that after adsorption it again turns into its original properties.

Table-6: Effect of point Zero Charge of activated Carbon

S.No	Initial pH	pH by adding adsorbent	pH at 24 hrs	pH at 48 hrs
1	1.97	1.99	2.07	2.02
2	2.56	2.61	2.89	2.66
3	4.02	4.45	5.04	4.68
4	8.53	6.34	5.8	5.75
5	10.63	8.15	7.65	7.23
6	9.59	7.12	6.21	6.07

5.4 Investigation of Thermodynamic Parameters

The effect of temperature on the adsorption capacity was determined by calculating the thermodynamic parameters like change in enthalpy ΔH^0 , entropy ΔS^0 and Gibbs free energy ΔG^0 which were evaluated by using the following equations:

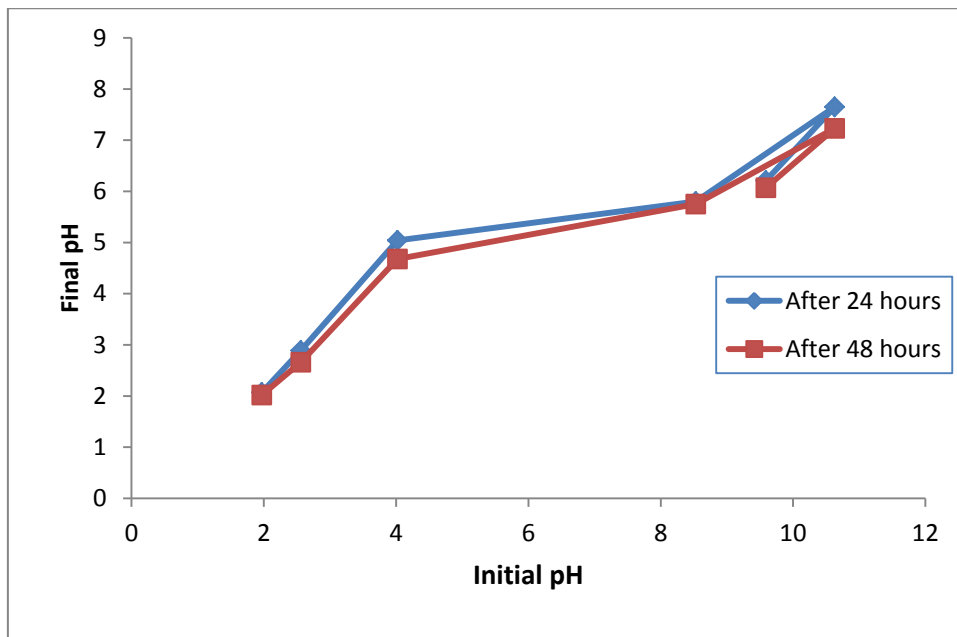


Fig-7: Effect of point Zero Charge of activated Carbon

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{----- (4)}$$

$$\ln k = \Delta S^0/R - \Delta H^0/RT \quad \text{----- (5)}$$

$$\Delta G^0 = -RT \ln k \quad \text{----- (6)}$$

Where R is the gas constant, T is the absolute temperature, k is the equilibrium constant. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the Van't Hoff plot of $\ln K_D$ versus $1/T$ as shown in Figure 8 and Table.7²¹.

The values of ΔG^0 were negative at all temperatures indicating that the adsorption of Ni on activated carbon was spontaneous process and its magnitude is shifted to a higher negative values as the temperature is increased indicating that the adsorption process is more spontaneously proceeded at higher temperatures. The negative values of ΔH^0 show the exothermic nature of the adsorption process. The positive value of ΔS^0 reflects the increased in randomness at the solid-solution interface and suggests some structural changes were bring about by adsorbent during the adsorption process²²⁻²³.

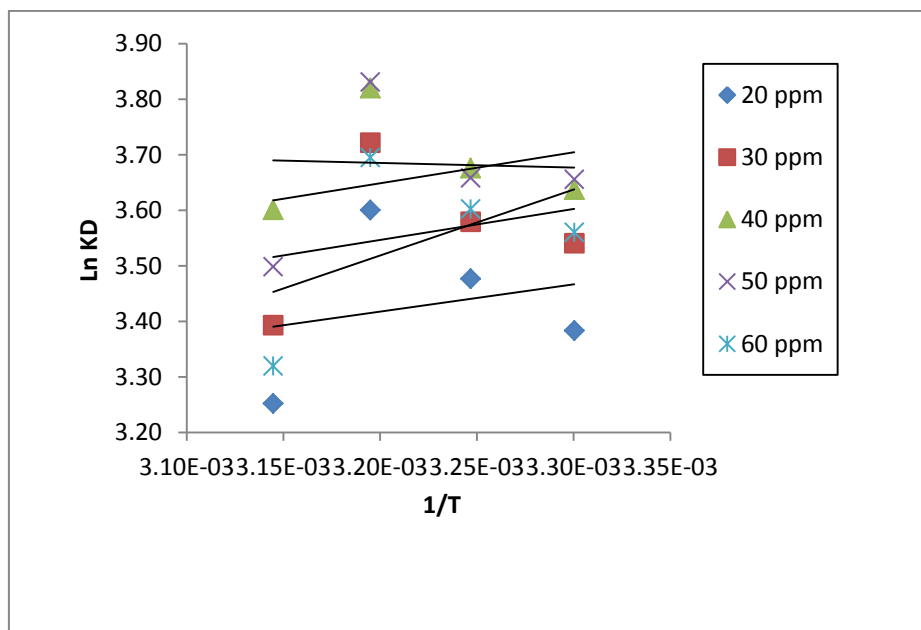


Fig-8: Plot $\ln K_D$ vs $1/T$ of Activated carbon-Ni System

Table-7: Thermodynamic parameters for the removal of Ni by using Activated carbon.

Adsorbent	Concentration (ppm)	ΔH° (kJ mol ⁻¹)	ΔS° (J deg ⁻¹ mol ⁻¹)	ΔG° (kJmol ⁻¹)			
				293K	303K	313K	323K
Activated Charcoal	20	-0.059	0.222	-0.126	-0.127	-0.128	-0.129
	30	-0.067	0.213	-0.130	-0.132	-0.133	-0.134
	40	0.010	0.475	-0.135	-0.138	-0.140	-0.143
	50	-0.067	0.225	-0.134	-0.135	-0.136	-0.137
	60	-0.143	-0.034	-0.152	-0.152	-0.152	-0.152

6. CONCLUSION

The industrial wastewater contains dissolved metals like mercury, lead, cadmium, molybdenum, copper, zinc and chromium due to different manufacturing processes. The present studies emphasize to design a model system to reduce the excess amount of toxic metals. Adsorption method was adopted for the minimization of contaminants to meet the discharge requirements. Activated carbon is known for its effectiveness in removing organic impurities, metal contaminants from water and wastewater. In the present work activated carbon was prepared from sugarcane bagasse and its carbonized forms were employed for the removal of Ni under the optimized adsorption conditions like optimization of amount of adsorbent, shaking time and concentration. It was found that about 99.99 % removal was achieved. The validity of adsorption process was evaluated by employing adsorption models like Freundlich and Langmuir. Thermodynamic feasibility, pH_{Zero} of the adsorption process was also evaluated. The impurities can be reduced by using low cost adsorbent and maintained the discharge limits as recommended by WHO.

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