Batch Adsorption Studies of Manganese by Wastes of Coconut Shells and Photocopier Toner

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Abstract: Due to the rapid industrialization many toxic metals were released in to environment by operations like Electroplating, Mining and also during the manufacture of paints, dyes, Motor Vehicles, etc. Manganese is one such toxic heavy metal released as effluent from industries. This work includes the removal of manganese from aqueous solutions using activated carbon from coconut shells and photocopier toner waste as adsorbents. Adsorption process was conducted in batch wise manner and parameters like Agitation time, Initial concentration of Adsorbate, Dosage of adsorbent, Size of Adsorbent, pH of solution were studied. From this experimental study, it was inferred that photocopier Toner waste was superior to Activated Carbon derived from coconut shells in adsorbing manganese from aqueous stock solution. For 0.5g of Activated Carbon at 1g/l of adsorbate concentration with an optimum agitation time of 110 minutes and pH at 3 was found to remove 38% of manganese where as Toner waste at the same prevailing conditions adsorbed 78% of manganese. Increase in dosage of adsorbent, decrease in adsorbent size, decrease in initial concentration of solution and acidic medium favored the adsorption phenomenon for manganese.

***Keywords* — *Adsorption, Activated Carbon, Colorimeter, Freundlich Isotherm, Langmuir Isotherm and Toner*.**

I. INTRODUCTION

Adsorption has great applications in industries and in waste water treatment techniques. "Adsorption is the accumulation of atoms, molecules or ions at the surface of a solid or liquid as a result of physical/chemical forces". The term equilibrium distribution depends on contact time in batch operation. So agitation time has great importance in batch adsorption studies. Adsorption is basically of 2 types based on the forces acting on it. Physical Adsorption (Physisorption), Activated Adsorption (Chemisorption). Some of adsorbents are Activated Carbon, Silica Gel, Zeolite, Activated Alumina, Fuller's Earth, etc. We can also use agricultural wastes as adsorbent like Treated Rice Husk, Saw Dust, Corn Cobs Powder, Coffee Waste, etc. Manganese is not only an essential component, when present in large quantities than the recommended levels it do acts as toxic compound. The permissible limit for manganese as an essential nutrient is (11mg/d), helps in our metabolism, if taken in excess results in adverse effects like forgetfulness, nerve damage, etc. The presence of excess manganese in environment does result in Surface, Ground and Sewage water contamination. Apart from these considerations Manganese has wide applications in iron and steel production, produces low-cost stainless steel formulations, and decolorizes glass. Some of the industries which release manganese as an effluent are Electroplating Industry, Paints and Dyes, Fertilizers, Motor Vehicles, Mining and Metallurgical Industries. Ameena Y.Khan (1) et al worked on adsorption of manganese ions from aqueous solution on to 3 different granular activated carbons treated with EDTA and its Sodium salt. Abdessalem Omri and Mourad Benzina (2) experimented on removal of manganese by adsorption using activated carbon derived from Ziziphus spina-christi seeds. B. Veena Devi(3) studied Adsorption of Chromium on Activated Carbon prepared from Coconut Shell. Biomass-waste derived activated carbon used for the removal of arsenic and manganese ions from aqueous solutions was studied by Budinova (4) et al. Manganese adsorption and Desorption in Calcareous Lebanese Soils was studied by Curtin (5) et al. Juan Carlos Moreno-Piraján(6) et al made investigation on the removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells. A Toner particle has 100 µm size with a weight of 1 nm. Production of nano particles was studied by Mallika Rani Parimi (7). Accumulation of Manganese by Citrus root adsorbent was studied by the scientists Morita shuji(10) by which the effect of heavy metals on the adsorption of manganese from solution was found in dead root of unshed and living root of trifoliate orange. P.Roccaro (11) et al made a study on the removal of manganese from water supplies intended for human consumption. Savova D (12) et al made a lab scale experimental study on the adsorption of manganese ions on Activated Carbons obtained from Olive Waste Materials. Theresa Feltes (13) et al made some trials on adsorption of manganese on cobalt catalyst.

ACTIVATED CARBON from coconut shells and Photocopier TONER waste were selected as adsorbents for this work. There is no literature available on the usage of

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these wastes as adsorbents for the removal of manganese. Here Activated Carbon is prepared from coconut shells by Carbonization process and used up Toner from photocopier machines were considered, without disturbing its commercial use. In this study, batch operation is chosen.

II. EXPERIMENTATION

A. Preparation of Activated Carbon (From Coconut Shells):

Activated carbon is carbon produced from carbonaceous source materials like nutshells, peat, lignite, etc. Activated Charcoal is prepared by physical reactivation process particularly by Carbonization from coconut shells.

Coconut shell is pyrolyzed at temperature in the range 600-900°C, in absence of air (usually under inert atmosphere (N_2, Ar)). The pyrolyzed powder is collected and sizing is done according to the need of the experimentation.

B. Preparation of Toner:

A Toner is typically composed of 80-90% plastic polymer and 10-20% carbon black pigment.

In our present study the used up toner from photocopier machine is taken.

C. Preparation of Manganese stock Solution:

In order to make Manganese stock solution 1g of $KMnO_4$ of A.R. grade is taken in to 1000ml of distilled water. The stock solution made is of the concentration of 1g/l.

D. Batch Adsorption Experiments:

All the adsorption experiments were done in batch mode for 110 min(Optimum contact time for adsorption of Manganese). The effect of initial manganese ion concentration(0.01- 1g/l), pH(3 - 12), dosage of adsorbent(0.1-0.5g) were studied by conducting experiments in a 250ml conical flask into which 50ml of 1g/l $KMnO_4$ solution is added .To this solution varying proportions of parameters were added accordingly for the study of each parameter, mechanically agitated in a rotary shaker. After filtration using a filter paper, Mn(II) ions remaining in the solution were determined by colorimeter. Optical densities were noted and the concentrations were obtained from the so generated standard curve (Calibration curve).

III. RESULTS AND DISCUSSION

A. BATCH ADSORPTION STUDIES:

1. Generation of calibration curve data:

Solutions of various manganese concentrations are prepared, calorimeter is calibrated and then the optical densities of varying concentrations were noted. A graph is drawn with Optical density vs. Concentration of $KMnO_4$ solution shown in fig.1.

2. Effect of agitation time (Activated Carbon and Toner):

11 flasks are taken, into which 50ml of 1g/l $KMnO_4$ solution with a pH of 3, 0.5g of 150-mesh sized adsorbent are added. Then all the flasks are continuously agitated in a rotary shaker. Sample is drawn for every 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 minutes. After adsorption, the adsorbent is filtered and the filtrate is collected. Samples are collected and optical densities are measured. Using the calibration curve, % removal of manganese is found. With increase in Time, % Removal of Manganese increases from 10 to 110 minutes. Optimal agitation time is 110 minutes. % Removal of Manganese at 110minutes is at a maximum of 77.5%. Hence the optimal agitation time was considered as 110minutes, is shown in Fig. 2 for both the adsorbents.

3. Effect of Initial Concentration of $KMnO_4$ solution (Activated Carbon and Toner):

10 flasks of different concentrations of $KMnO_4$ solutions are taken 1, 0.8, 0.6, 0.4, 0.2, 0.1, 0.07, 0.05, 0.03, 0.01g/l respectively. 50ml solution of each concentration with pH at 3 is taken; 0.5g of the adsorbent (150-mesh size) is added to the flask. Now all the flasks are kept for shaking for 110 minutes. After adsorption, optical density for each concentration is noted. For Activated Carbon, with increase in Initial Concentration of $KMnO_4$ solution the % removal decreases. At a concentration of 1g/l of $KMnO_4$ solution the % removal is only 37.2%, at 0.01g/l of $KMnO_4$ solution it is 84%. For Toner, at a concentration of 1g/l of $KMnO_4$ solution the % removal is 77.5%, at a concentration of 0.01g/l of $KMnO_4$, % removal is 90%. At low initial concentrations of $KMnO_4$ the % removal is more compared to the higher concentrations shown in fig.3.

4. Effect of Size of Adsorbent (Activated Carbon):

Take 5 flasks into which we add 50ml of 1g/l of $KMnO_4$ solution with pH at 3. Add 0.5g of adsorbent of varying sizes (6, 10, 36, 85, 150 meshes) and kept shaking for 110 minutes in an orbital shaker. For Activated Carbon, it is seen that with an increase in mesh size of Adsorbent the % Removal increases. When the mesh size was around 6 μm % removal is 4.5%, at 150 μm it is 37.2%.The optimum size for adsorption is 150-mesh sized adsorbent.

5. Effect of Dosage of Adsorbent (Activated Carbon and Toner):

5 flasks are taken of each with 50ml of 1g/l $KMnO_4$ solution, with pH maintained at 3.To these flasks we add adsorbent of 150-mesh size of varying amounts of 0.1, 0.2, 0.3, 0.4, 0.5g respectively, kept for agitation for 110 minutes. With increase in dosage of adsorbent the % removal increases. At 0.1g of the adsorbent the % removal is only 2%, at 0.5g it is 39%. So, the optimum dosage of Activated Carbon is 0.5g. For Toner, at 0.1g % removal is 37.2%, at 0.5g % removal is 78%. So, the optimum dosage

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was 0.5g and the comparison plot showing this adsorbent dosage is fig.4.

6. Effect of pH of Solution (Activated Carbon and Toner):

5 flasks each of 50ml of 1g/l concentration of $KMnO_4$ solution are taken and the pH (3, 5, 9, 11, and 12) of each flask is varied. To these flasks 0.5g of 150-mesh size adsorbent is added and kept shaking for 110 minutes. An increase in pH of the solution decreases the % removal. For pH range from 3 to 12, Activated Carbon removes manganese from 38% to 4.5%, for Toner it is 84% to 7%. We can see this study in fig.5.

B. ADSORPTION ISOTHERMS:

1. Freundlich Isotherm:

Freundlich isotherm is given by:

$$Q_e = K_f C_e^n \quad (1)$$

In logarithmic form:

$$\mathrm{Log}Q_e = \mathrm{Log}K_f + n\mathrm{Log}\ C_e \quad (2)$$

K_f and n are the Freundlich constants,

Q_e is the metal uptake given by:

$$Q_e = \frac{V(C_i - C_e)}{1000W} \quad (3)$$

From fig.6 it is observed that Freundlich Isotherm fits for the present condition with

$$\mathrm{Log}Q_e = 0.731\mathrm{Log}C_e - 1.071 \quad (4)$$

From which we get

$K_f = 0.0849$, n = 0.731

R^2=0.867 which is favorable.

From fig.7 it is observed that Freundlich Isotherm best fits the experimental data for Toner, given by

$$\mathrm{Log}Q_e = 0.813\mathrm{Log}C_e - 0.467 \quad (5)$$

$K_f = 0.3412$, n = 0.813

R^2=0.987 is favorable.

2. Langmuir Isotherm:

The linear form of Langmuir isotherm is given as:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (6)$$

From this Langmuir Isotherm, the parameters Q_m and b are calculated by making a plot of C_e/Q_e vs C_e.

Fig.8 says that Langmuir Isotherm does not fit the experimental data.

The expression obtained for Activated Carbon is:

$$C_e/Q_e = 19.4Ce + 3.499 \quad (7)$$

From which we get Q_m = 0.0515, b = 5.5494, R^2 = 0.754.

So, it is not a favorable condition.

From fig.9 it is observed that Langmuir Isotherm does not fit the experimental data.

The expression we obtained for Toner is:

$$C_e/Q_e = 7.980Ce + 1.042 \quad (8)$$

From the above Langmuir plot we get Q_m = 0.1253, b=7.6591.

R^2=0.934 is not favorable condition.

C. Comparative Study:

Mamdouh M. Nassar (8) et al investigated on adsorption using low cost materials like palm fruit bunch and maize cob, % removal of manganese is 57 – 79% and 60 – 79% respectively for varying concentrations of $KMnO_4$ solution(1-10mg/l). Maria G. da Fonseca (9) et al studied adsorption of manganese from aqueous solution using clay material and observed the adsorption quantity of Mn^{2+} ions to be around 0.52mmol/g. In this study, activated carbon prepared from coconut shells and photocopier toner waste was used as adsorbents to remove manganese. The observed % removal was 38% and 78%, adsorption quantity of Mn^{2+} ions are 7.922mol/g and 7.635mol/g respectively at 1g/l. From these comparative studies it was concluded that photocopier toner waste can be used as a good adsorbent for removing manganese ions from aqueous solutions than palm fruit bunch, maize cob, clay materials.

IV. FIGURES

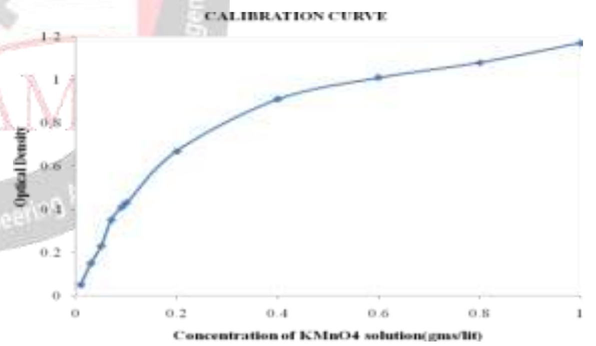

Fig.1. Calibration Curve

Fig.1 serves as reference plot to find the concentration of $KMnO_4$ at respective optical densities.

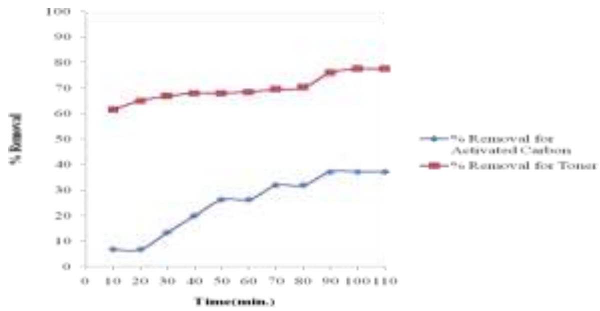

Fig.2. Comparison for Activated Carbon and Toner regarding agitation time

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Fig.2 says that with increase in agitation time, % removal of manganese increases and reaches to a point where all the pores of the adsorbent gets clogged by the metal ions after which observable change is not seen. % removal of manganese using Toner is observed to be maximum at 77.5% and 38% for Activated Carbon. So, optimum agitation time is 110minutes.

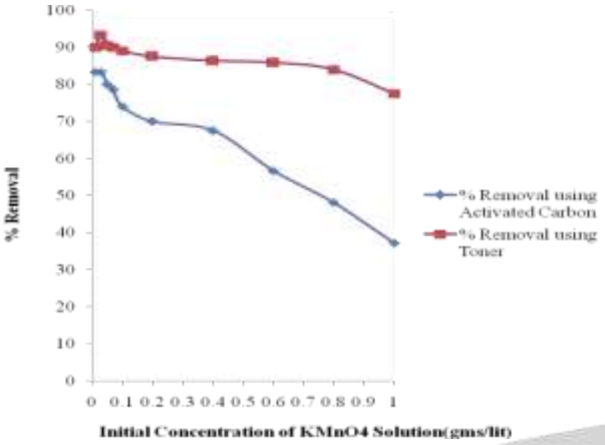

Fig.3.Comparison of Activated Carbon & Toner regarding initial concentration of $KMnO_4$ solution.

From fig.3., it is inferred that at low initial concentrations of $KMnO_4$ the % removal is more compared to the higher concentrations. For Activated Carbon at 0.01g/l of $KMnO_4$ solution it is 84%. For Toner, it is 90%.

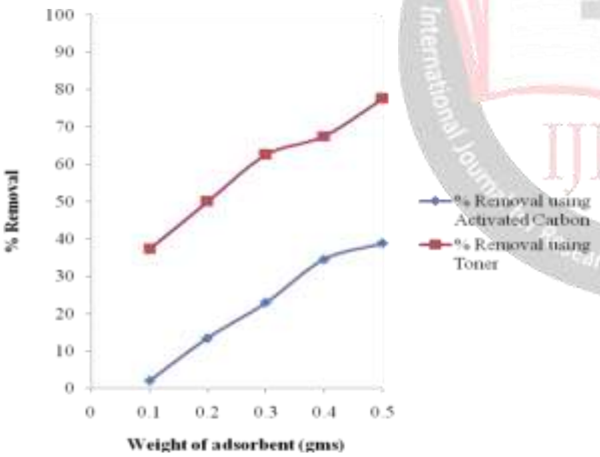

Fig.4. Comparison for Activated Carbon & Toner for dosage of adsorbent

As the dosage of adsorbent increases, adsorption increases. From fig.4., it is seen that % removal of manganese increases from 2% - 39% for 0.1g - 0.5g of Activated Caron and 37.2% - 78% for 0.1g - 0.5g of Toner respectively. So, the optimum dosage was found to be 0.5g.

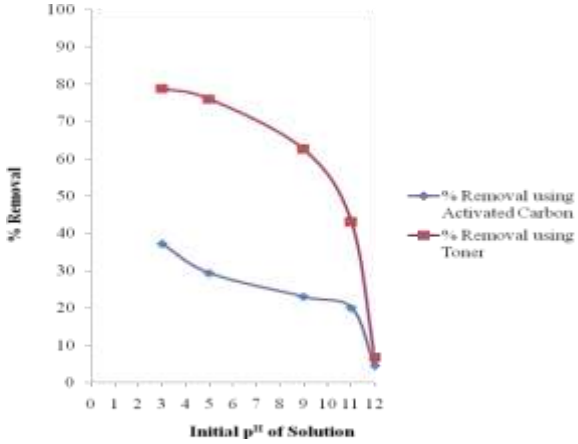

Fig.5. Comparison for Activated Carbon & Toner considering pH of Adsorbate

An increase in pH of solution decreases the % of manganese ions removed and this is seen in fig.5. For pH range from 3 to 12, Activated Carbon removes manganese from 38% to 4.5% and Toner from 84% to 7%. So, acidic medium favors the process.

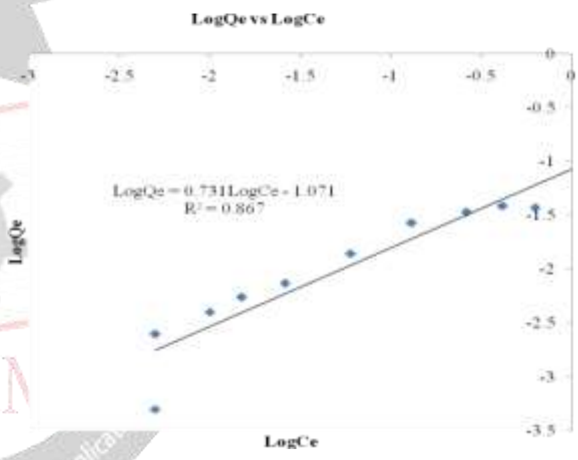

Fig.6. Freundlich Isotherm for Activated Carbon.

From fig.6., Correlation coefficient is found to be R^2=0.867.Freundlich isotherm best suits the adsorption process.

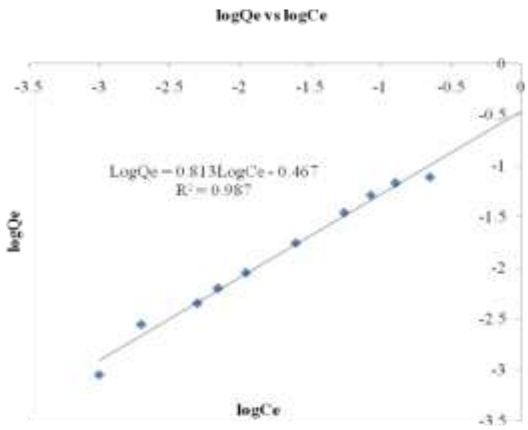

Fig .7. Freundlich Isotherm for Toner

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From fig.7., correlation coefficient for Toner is R^2=0.987. As very high coefficients are observed, Freundlich isotherm is considered as the best suited one.

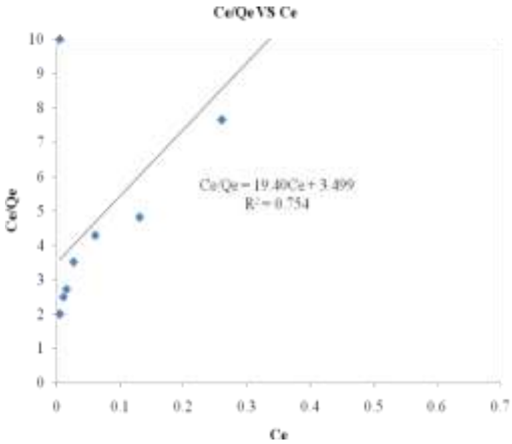

Fig.8. Langmuir Isotherm for Activated Carbon

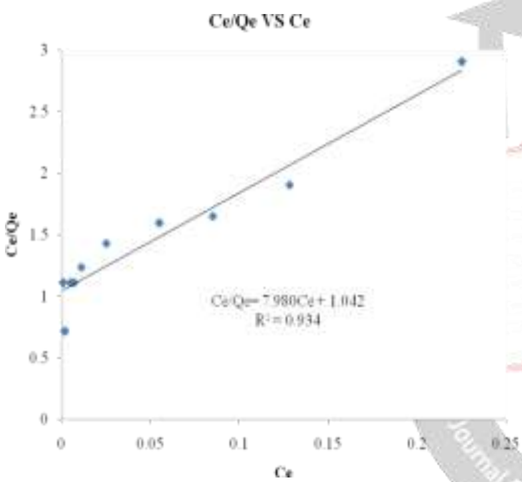

Fig.9. Langmuir Isotherm for Toner

From figures 8&9, Correlation coefficients are R^2 = 0.754 for Activated Carbon and R^2=0.934 for Toner.

V. CONCLUSION

Among Activated Carbon from coconut shells and photocopier Toner waste, Toner waste was considered as the best adsorbent for its good adsorption capacity in removing manganese from aqueous solution. Batch adsorption studies were performed and it was observed that with an increase in dosage of adsorbent, decrease in particle size and concentration of stock solution, the % removal of manganese increased. For Activated Carbon from coconut shells, the % removal is nearly 38% where as that for Toner it is 78%. Of the two Adsorption Isotherms, Freundlich Isotherm suits best for both the adsorbents Activated Carbon and Toner. Optimum conditions observed from this adsorption study were pH – 3, dosage of adsorbent – 0.5g, agitation time – 110minutes, concentration of $KMnO_4$ solution taken - 1g/l, 150 mesh sized adsorbents were chosen. From all the above considerations and comparisons Toner waste was considered to be more preferable than Activated Carbon for adsorption of manganese.

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APPENDIX

b	-	Langmuir constants
C_e	-	Concentration of adsorbate at equilibrium, g/l
C_i	-	Initial concentration of $KMnO_4$ solution, g/l
EDTA	-	Ethylene Diamine Tetra Acetic acid
$KMnO_4$	-	Potassium Permanganate
MnO	-	Manganese Oxide
MnO_2	-	Manganese dioxide
$MnCO_3$	-	Manganese Carbonate
n	-	Adsorption intensity, Freundlich Constant
Q_e	-	Equilibrium metal uptake
Q_m	-	Maximum amount of manganese adsorbed
R^2	-	Regression Coefficient
V	-	Volume of the sample stock solution, ml
W	-	Amount of adsorbent taken, g

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