

REMOVAL OF PHENOL FROM WASTE WATER USING MAGNETIC IRON OXIDE LOADED IN ACTIVATED CARBON

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Abstract - Adsorption of organic and inorganic molecules on activated carbon is one of the classical and best studied methods in separation science and application in a variety of fields. The process involved is essentially phase separation of target compounds from solution or gas phase to solid. Contacting the solid with the medium under optimal flow conditions. The application of activated carbon in the flow through mode is limited to powdered activated carbon. The adsorption dynamics are very favourable, but the challenge is in separating the fine particles after adsorption. If this stage is made more operator friendly and cost effective, powdered activated carbon will be a preferred material, especially in large scale flow- through applications. Preparation of a magnetic iron oxide activated carbon composite that has magnetic properties. The idea behind a magnetized activated carbon is that it could be recovered using non-invasive methods. As part of this work procedures were evolved to prepare magnetized activated carbon samples with different iron oxide loading. Physical and chemical characterization of a new material is very important to understand its desired properties. In this work the adsorption features of activated carbon and the magnetic properties of iron oxides were combined in a composite to produce magnetic adsorbents. These magnetic particles can be used as adsorbent for a wide range of contaminants in water and can subsequently be removed from the medium by a simple magnetic procedure. Activated carbon with iron oxide magnetic composites were prepared and characterized.

Key Words: Magnetised granular activated carbon, Phenol, Adsorption, Magnetic iron oxide

1. INTRODUCTION

Adsorption processes for water treatment have had a long and productive history. The use of carbon extends so far back into history that its origin is impossible to trace. Charcoal was used for drinking water filtration by ancient inhabitants in India and carbonized wood was used as a medical adsorbent and purifying agent. (Cheremisinoff, P.N. 1980). One of the later adsorption applications is purification, such as the removal of H₂S and obnoxious fumes from air and the removal of organic compounds from liquid water. Activation is a term generally used to refer to the Overall reactions can be split into two steps, Carbonization and Oxidation. The treatment of contaminated effluents is an increasing problem in recent times. One of the major methods for the removal of pollutants from waste water is using porous solid adsorbents. The properties of porous

solids that render them useful for water treatment include high porosity and surface area as well as the physical and chemical nature of the internal adsorptive surfaces. The mode of application of activated carbon depends on their physical forms and dimensions. The main objective of the study includes the preparation of a new activated carbon material that can be separated from treated waters using a magnetic separation procedure.

2. PREPARATION OF BASIC SAMPLES

2.1 Granular Activated Carbon (GAC)

Carbon granules collected on sieve no. 120 and passing through 80 were selected for this study. In order to remove alkaline impurities, samples were further washed with dilute hydro chloric acid (0.1N) and treated with dilute sodium bicarbonate solution (0.1N) to remove any excess acid. Carbons were again washed thoroughly with distilled water until the washings gave neutral pH values. The GAC was then dried at 150°C in a hot air oven for 3 hours and stored in an air tight PVC based containers and kept in a desiccator.

2.2 Magnetic Iron Oxide (MIO)

The pure magnetic iron oxides were prepared. 80g of ferrous sulphate was dissolved in 560mL of distilled water. Approximately 1g of hydrazine sulphate was added to this solution. The solution was kept on a hot plate to boil 6.5g of potassium nitrate and 45g of potassium hydroxide was dissolved in 240mL of distilled water in another beaker. Around 1g of hydrazine sulphate were added to remove any traces of dissolved oxygen. This solution was added to the hot ferrous sulphate solution with constant stirring.

3. METHODOLOGY

3.1 pH

pH of the magnetic iron oxide activated carbon composites was determined by ASTM D3838 method.

Sample of composites equivalent to 10 g on a dry basis was weighed and transferred to a boiler flask. Approximately 110mL of distilled water was brought to boiling and 100mL of this was immediately added to the boiler flask containing the sample and allowed to boil for 900 s. The flask was then removed from the hot plate and contents were filtered immediately through the filter paper

premoistened with distilled water used for the test. The filtrate was cooled to 50°C and pH was measured using a digital pH meter.

3.2 Total Ash

The total ash content of the samples was determined by ASTM D2866 method. The crucibles used for the study were pre-weighed by igniting in the muffle furnace at 650 °C for 1 hour and cooling by keeping in a desiccator to room temperature followed by weighing to the nearest 0.1mg. An adequate sample of the composites was dried to constant weight. A sufficient amount of sample to get an ash content of 0.1g was weighed out to the nearest 0.1 mg into pre-weighed crucibles and ignited in the furnace at 650°C for 3h. The crucibles were then cooled in a desiccator and determined the weights.

3.3 Absolute Density

Absolute density of the prepared samples was estimated by displacement method using nitrobenzene. A clean dry specific gravity bottle was weighed accurately using the analytical balance. Approximately one gram of the sample was added to the bottle and weighed again to find the weight of sample and specific gravity bottle together. Then the bottle with carbon sample was filled with nitrobenzene and weighed again. The bottle was then cleaned, dried and filled with nitrobenzene and weighed. The following equation was used for calculating the absolute density.

$$A.D = \frac{W1 - W_o}{(W3 - W_o / 1.2) - (W2 - Wt. / 1.2)}$$

Where,

1.2 = Specific gravity of nitrobenzene

W_o = Weight of specific gravity bottle

W₁ = Weight of specific gravity bottle +
sample

W₂ = Weight of specific gravity bottle +
sample + nitrobenzene

W₃ = Weight of specific gravity bottle +
Nitrobenzene

3.4 Iron Oxide Loading

The amount of iron oxide loaded onto different composites was determined by standard gravimetric protocol. 1g of the sample was weighed out into a clean 250mL glass beaker. 50 mL of hydrochloric acid was added to it and stirred well to dissolve iron oxide from the composites. The mixture was then filtered through a Whatman No. 1 filter paper to separate the carbon particles. Approximately 2mL of concentrated nitric acid was then added to the filtrate followed by 200mL of distilled water. The contents were then kept over a hot plate and allowed to boil for approximately 5 minutes. To the hot solution, containing dissolved iron, concentrated ammonia solution

was added till excess with constant stirring. Then the precipitate was allowed to settle. The supernatant solution was decanted and the precipitate was washed with hot 1% ammonium nitrate solution until the washings were chloride free. The solution was then filtered through a Whatman No. 1 filter paper to collect the precipitate. The precipitate was then placed on a pre-weighed crucible and ignited to red hot temperature to get residue. The amount of iron oxide loaded on each composite in terms of iron (Fe) was determined from the weight of residue obtained.

4. BASIC EXPERIMENTAL RESULTS

1. The pH of the waste water sample was determined using pH meter is 8.5
2. Total amount of volatile and nonvolatile substance present in the sample is 118 mg/L and 14 mg/L respectively.
3. Absolute density of the sample is 2.36 g/cm³

5. PHENOL CHARACTERISTICS

5.1 The phenolic pollution and toxic effects

Application of products containing a high concentration of phenol to the skin causes blisters and burns on the skin; heart, kidneys, and liver damage may occur with exposure to high levels of phenol. Other effects of chlorophenol poisoning include damage to the liver, kidneys, lungs, skin and the digestive tract.

Phenol is the major pollutants in the wastewater from various industries. The phenolic pollution is commonly observed in the chemical and pharmaceutical industries like petro chemical industries, petroleum refineries, coal gasification, liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills and pharmaceutical industries. It is a highly corrosive and nerve poisoning agent. When these pollutants contaminate the groundwater, rivers and reservoirs, which are sources for human consumption, harmful side effects, such as sour mouth, diarrhea, excretion of dark urine and impaired vision are seen. The toxic levels usually range between the concentrations of 10-24 mg/L for human and the level for fish is between 9-25 mg/L. Environmental Protection Agency, EPA has set a limit of 0.1mg/L of phenol in waste water, while that in drinking water is 0.002 mg/L. A total dose of 1.5 gm may be fatal.

5.2 Adsorption

Adsorption is considered as one of the appropriate techniques for removal of phenolics from water because the technique is easy to design and operate. Efficiency of the adsorption process is governed by; Adsorbent's properties, i.e. its functional group composition, the size of its surface area together with the distribution of the pore size and the extent of its ash content. The solution chemistry including its

pH, temperature, availability of other solutes competing for the adsorbent surface area and the concentration of the adsorbate, nature of the adsorbate. This includes its degree of solubility in water, size and molecular weight. Reference found phenol adsorption process to be solely dependent on the initial pollutant, which in turn depends on pH of the solution. Adsorption of pollutants from water is believed to be based on the following steps:

1. Movement of the pollutant molecules towards the adsorbent across the external boundary layer.
2. Movement of the pollutant molecules to the adsorbent's active surface sites.
3. Adsorption of the pollutants on the active surface sites.
4. Migration of the adsorbed pollutants through diffusion onto the pores surfaces.

6. EXPERIMENTAL INVESTIGATIONS

6.1 pH

The pH of the carbon samples was determined using a digital pH meter as per the procedure given in methods. The obtained values for GAC, MGAC1, MGAC2 and MGAC3 are 7.2, 6.8, 6.9 and 7.1 respectively. The analysis of the four samples was done and the results are given in Chart-1.

Table - 1: Obtained pH values of samples

Sl. No.	GAC	MGAC1	MGAC2	MGAC3
pH	7.2	6.8	6.9	7.1

However, it is known that the adsorption of phenol compounds depends on the pH of the carbon surface (Solar, J. M., 1987).

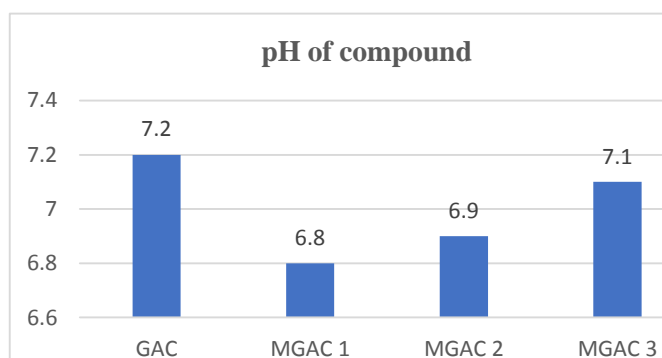


Chart - 1: pH on Composite samples

The carbons were neutralized during the washing process. The pH of activated carbons has a direct relation to the concentration of oxygen bearing surface functional group present. However, in this study chemical treatment followed by washing during the preparation setup of rendered carbons with neutral surface pH. The neutral values indicate the absence of any basic and acidic impurities.

6.2 Total Ash

Activated carbon contains inorganic components as part of the source material, or the ash may originate from chemicals added during activation. It has generally been seen that the total amount of inorganic constituents will vary from one adsorbent to another (Brady, M. & G. McKay., 1995). The ash content of carbon is a factor affecting performance of activated carbon in water treatment, especially the iron content (Faust, S. D. & Aly, O. M., 1987). Hence, the estimation of total ash content of the adsorbent samples is important to understand its performance in water treatment.

Table - 2: Obtained Total ash content values of samples

Sl. No.	GAC	MGAC1	MGAC2	MGAC3
TOTAL ASH (%)	3.72	12.1	18.6	24.7

The analysis of GAC showed a total ash content of 3.72%. The values obtained for MGAC1, MGAC2 and MGAC3 are 12.1, 18.6 and 24.7% respectively. The analysis of the four samples was done and the results are given in Chart-2.

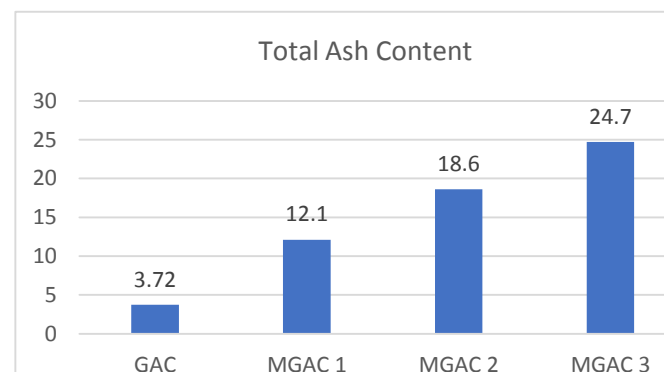


Chart - 2: Total ash content on composite samples

The control carbon GAC has similar ash content to previously reported data on various carbons. The final residue of ignition of these samples will constitute ash from the oxidation of carbon and iron oxide, Fe₂O₃. The increased ash content in these modified samples will have a negative influence on their adsorption capacity. The inorganic content in these modified samples can reduce adsorption compared to the control carbon. The reports also suggest that the value can vary from 2 to 30 % in various commercial products.

The low value of ash content in GAC suggests a better adsorption capacity and performance. The increase in the total ash content in MGAC1, MGAC2 and MGAC3 is expected due to the incorporation of iron into the carbon matrix.

6.3 Iron Loading

The iron oxide impregnated on modified carbon samples was determined by gravimetric procedure. During the preparation, the concentration of chemicals (FeSO₄ and KOH) was calculated on a theoretical basis that can give an

approximate loading of iron oxide for each sample. So, it is important to determine the exact concentration of iron oxide actually loaded onto these samples. The analysis of the four samples was done and the results are given in Chart-3. The control carbon has zero iron concentration as the traces of inorganic iron that might be present could not be determined using the gravimetric procedure. Hence the iron loading on control carbon, GAC was taken as zero. The iron loading (in % Fe) in MGAC1, MGAC2 and MGAC3 were determined to be 5.19, 10.2 and 13.6 respectively.

Table - 3: Obtained Iron loading values of samples

Sl. No.	GAC	MGAC1	MGAC2	MGAC3
IRON LOADING (%)	0	5.19	10.2	13.6

The actual iron loading is much less compared to the theoretically predicted loading from the concentration of the chemicals used. The sample identity of activated carbon and magnetic iron oxides loaded composites are defined as GAC with zero iron oxides, MGAC1 with 5.19% iron loading, MGAC2 with 10.2% iron loading and MGAC3 with 13.6% iron loading. A previous study on magnetic composites with activated carbon has reported Fe₂O₃ concentration on loaded samples to be 25 to 47 wt. % (Oliveira, L. C. A. *et al.*, 2002).

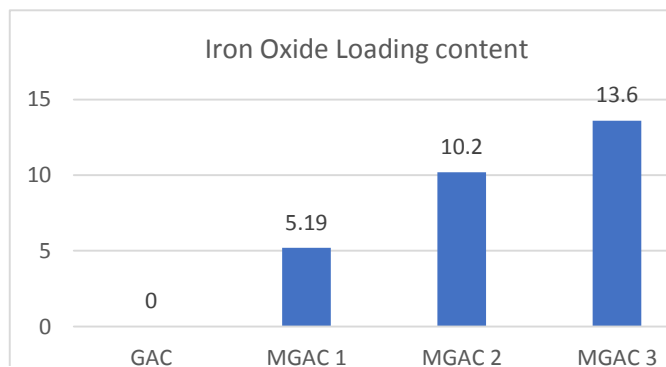


Chart - 3: Iron Oxide Loading on Composite Samples

The high values reported should be attributed to the free iron oxide that was precipitated in the bulk of the solution. The equilibration was completed within 2 hours and an additional equilibration time never resulted in an increase in the iron oxide loaded.

Also, an increased concentration of ferrous ion also failed to give an increased iron loading inside the pore structure since the pores were already saturated with the ferrous ion.

6.4 Iodine Number

The iodine number is defined as the number of milligrams of iodine adsorbed by 1 g adsorbent, when the iodine concentration of the residual filtrate is 0.02 N. Basically, Iodine number is a measure of the iodine adsorbed in pores and, is an indication of the pore volume available in the activated carbon of interest. The results are given in Chart -4.

Table - 4: Obtained Iodine number values of samples

Sl. No.	GAC	MGAC1	MGAC2	MGAC3
IODINE NUMBER	1018.23	874.7	831.16	602.51

The control carbon, GAC has an iodine number of 1018.23 where as iron oxide impregnated composite samples MGAC1, MGAC2 and MGAC3 have iodine numbers of 874.7, 831.16 and 602.51 respectively.

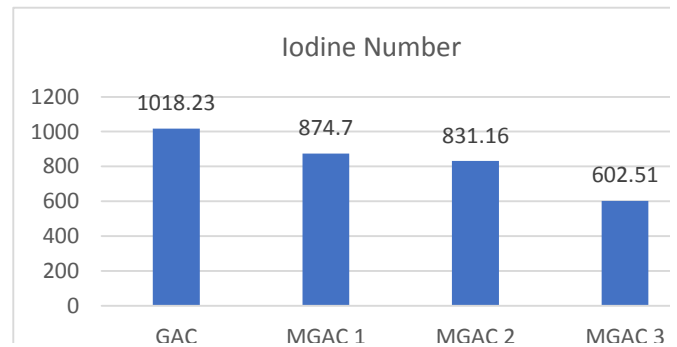


Chart - 4: Iodine Number Content on Composite Samples

Typically, carbons for water treatment have iodine numbers ranging from 600 to 1100 (Wagner, N. J. & Jula, R. J., 1981). The high value of iodine number for GAC indicates that the control carbon has high pore volume and is comparable to other commercial carbons. The loss in iodine number is not proportional to the iron loading. The values indicate that the adsorption capacity will decrease with iron loading. There is a sharp decline in the iodine number with increase in the iron loading indicating a reduction in the available pore volume. With respect to the control carbon, there is a 14.1 % reduction in iodine number in MGAC1. The corresponding reduction in iodine number for MGAC2 and MGAC3 are 18.4% and 40.8% respectively. The higher reduction in pore volume in MGAC3 is mainly due to the increased loading of iron oxide (13.6%) but is not proportional with reduction in other composite samples.

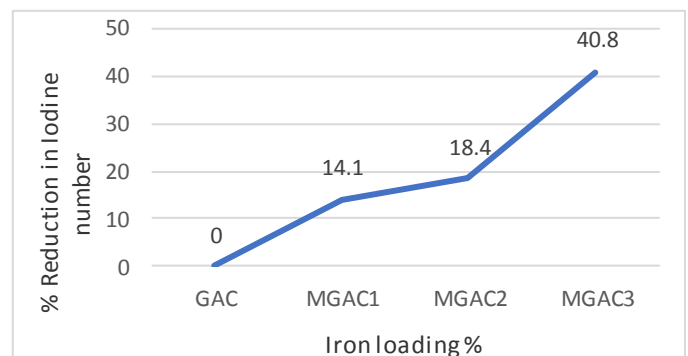


Chart - 5: Reduction in iodine number with respect to the control carbon

6.5 Absolute Density

The absolute density of the adsorbents is determined using a calibrated specific gravity bottle and solvent (nitrobenzene) that is capable of penetrating the pores of the adsorbent and whose density is accurately known. The absolute density for GAC, MGAC1, MGAC2 and MGAC3 were determined to be 1.29, 1.75, 2.05 and 2.2g/cm³ respectively. Analysis of some commercial activated carbon samples has shown that the real density can be as high as 2.1g/cm³.

Table – 5: Obtained Absolute Density values of samples

Sl. No.	GAC	MGAC1	MGAC2	MGAC3
Absolute Density (g/cm ³)	1.8	1.65	1.5	1.2

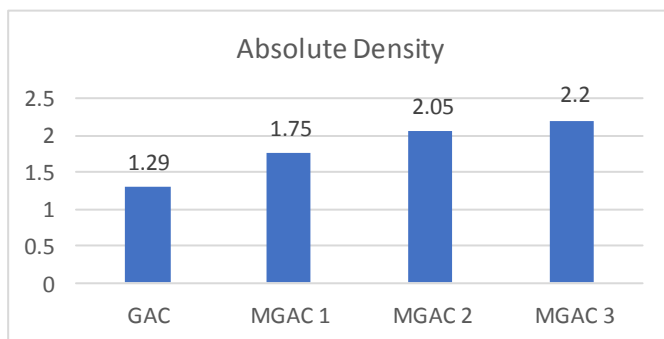


Chart – 6: Absolute Density of Composite Samples

The reported apparent density values of some commercial samples range from 0.18 to 0.53 g/cm³ (Netzer, A., & D. E. Hughes., 1984). The absolute density increases with the iron loading. This is expected as the impregnated iron oxide will increase the density of the sample. And this suggests that the increase in the absolute density is due to the iron oxide impregnated inside the pores of the carbon matrix. Hence the increased absolute density and correspondingly better settling properties of the impregnated activated carbon composites make it more technically feasible adsorbent which can be employed in wastewater treatment.

7. RESULTS AND DISCUSSIONS

7.1 Adsorption of Phenol on Activated Carbon Magnetic Iron Oxide composites

The concentration of phenols in wastewater varies from 10 to 3000 mg/L (Nemerow, N. L. & Dasgupta, A., 1991). Study of adsorption parameters from solution of non-electrolytes by micro porous solids is of great significance. The need for efficient removal of organic pollutants is becoming increasingly important. In this section an attempt is made to study the adsorption characteristics of phenol on the newly prepared activated carbon magnetic iron oxide composites. The objectives of this study are to evaluate the adsorption capacities of the composites towards phenol.

7.2 Spectrophotometric results

7.2.1 Procedure:

1. Set the wavelength to the value corresponding to maximum absorbance.
2. Place the cuvette or test tubes with same solution but at an unknown concentration.
3. Read the absorbance and the concentration for this wavelength.
4. Repeat the same procedure for a second solution.



Fig – 1: Spectrophotometer

7.2.2 Results

The results obtained from the samples in 30 minutes, 2 hours, 5 hours and 10 hours are given in the table below:

Table - 6: Concentration of phenol from samples

TIME (Minutes)	% Removal of phenol in samples			
	GAC	MGAC 1	MGAC 2	MGAC 3
30	74	86	91	94
120	76	87	93	97
300	78	89	93	98
600	78	89	93	98

7.2.3 Adsorption Kinetics

The reaction rate of adsorption of organic molecules is described by the solute uptake rate that determines the residence time required for the sorption reaction. It is well established that the sorption kinetics ultimately controls the process efficiency. The kinetic studies of phenol adsorption on GAC, MGAC1, MGAC2 and MGAC3 were carried out at a fixed initial concentration of 300 mg/L with adsorbent at different interval of time. The kinetic plots of phenol adsorption onto four adsorbents are given in Chart - 7. The amount of phenol adsorbed per gram of the adsorbent is plotted against time. The initial stage is very rapid and is followed by a slower adsorption step that gradually approaches an equilibrium condition.



Fig - 2: The samples after 300 minutes

Table -7: Percentage adsorption of phenol in samples

TIME (Minutes)	% of Adsorption of phenol in samples			
	GAC	MGAC 1	MGAC 2	MGAC 3
30	44	86	91	94
120	76	87	93	97
300	78	89	93	98
600	78	89	93	98

At first 30 minutes, a fraction of 74% phenol adsorbed is removed by GAC where as the corresponding values for MGAC1, MGAC2 and MGAC3 are 86%, 91% and 94%.

In 2 hours, the adsorption proceeds slowly with a small fraction of phenol reaching only 76% phenol adsorbed is removed by GAC where as the corresponding values for MGAC1, MGAC2 and MGAC3 are 87%, 93% and 97%.

In 5 hours, the adsorption proceeds slowly with a small fraction of phenol reaching only 78% phenol adsorbed is removed by GAC where as the corresponding values for MGAC1, MGAC2 and MGAC3 are 89%, 93% and 98%. This is because fast internal diffusion into the carbon matrix is hindered by the presence of iron oxide in the porous structure.

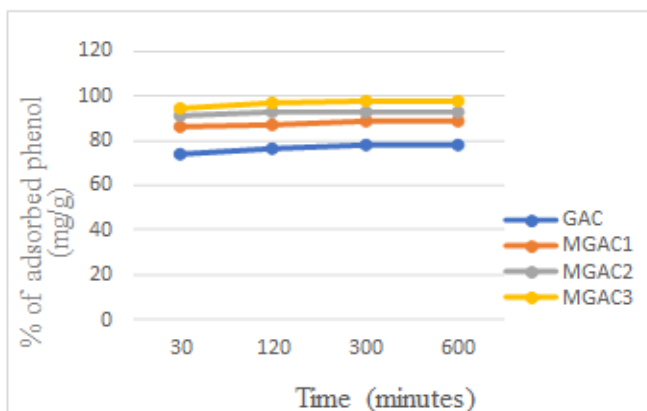


Chart - 7: Plot of phenol adsorption studies

Within 10 hours, the fraction of phenol adsorbed on GAC is 78%. Corresponding values for MGAC1, MGAC2 and MGAC3 are 89%, 93% and 98%.

This suggests that time does not have any significant influence on the fraction of adsorbate adsorbed in the initial

stages of the process. But the changes in the pore structure due to iron loading do have an influence on the initial uptake of phenol.

7.3 Separation Process

One of the major unit operations in any industry is the separation process. The weight of the carbon particles collected on the filter paper was determined. The percentage retention efficiency of the process was determined using the equation:

$$\% \text{ Retention Efficiency} = \frac{W1 - W2}{W1} \times 100$$

W1

where, W1 = Weight of the carbon added (0.5g)

W2 = Weight of the carbon that flowed out of the Settling column

In this study, this gave the rate constant for the limiting step in the phenol adsorption on carbon samples. These results show that iron oxide impregnation has lowered phenol adsorption rate on activated carbon. There is no prominent influence of temperature. The percentage retention of carbon particles in the settling column was in the order GAC < MGAC1 < MGAC2 < MGAC3.

The iron oxide on the activated carbon matrix has increased the absolute density of the composite sample and the increase is in proportion to the amount of iron oxide loaded. The percentage retention of carbon particles in the settling column was in the order GAC < MGAC1 < MGAC2 < MGAC3. The iron oxide impregnation on the activated carbon matrix has increased the absolute density of the composite sample and the increase is in proportion to the amount of iron oxide loaded.

Table - 8: Difference in the % retention of particles

Samples	W1	W2	% Retention
GAC	0.5	0.205	59
MGAC 1	0.5	0.24	52
MGAC 2	0.5	0.28	44
MGAC 3	0.5	0.29	42

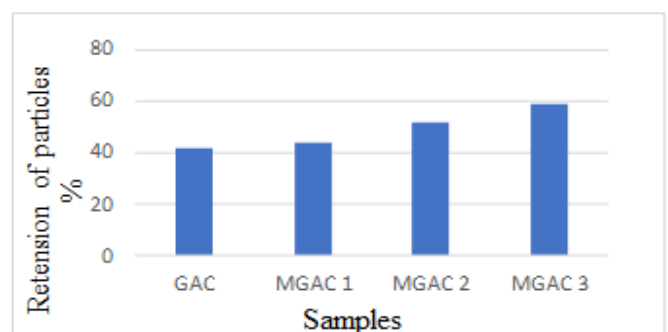


Chart - 8: Particles retained in the settling column

It is clear that as the particle size gets smaller, less amount of carbon particles was retained in the column. The dependence of percentage retention of particles in the settling column was studied using particle size between 88 to 125 microns. It is evident that as the particle size decreases the influence of iron oxide loading on the retention efficiency was reduced. The % of particles retained in the column is drastically reduced at higher flow velocities.

8. SUMMARY AND CONCLUSIONS

The suitability of magnetic iron oxide loaded activated carbon for the adsorption and subsequent separation of the adsorbent by retention were investigated and the effects of magnetic iron oxide (MIO) deposited on GAC on the physio-chemical properties were also investigated. The presence oxides of iron in various proportions. The structural environment and proportion of iron oxide varied depending on the sample. MIO was deposited inside and outside the pores.

The crystallites of MIO had size distribution corresponding to the pore diameter. The surface area determined and solution adsorption decreased with increasing MIO loading. The decrease in adsorption properties could not be directly correlated to the iron oxide content. This may be due to the variability in the chemical characteristics and particle size distribution of the mixed oxide. Corresponding to the decrease in the surface area due to the MIO loading there is a decrease in the adsorption frequency for the solute loading. The advantageous property of MIO-GAC is that after effecting adsorption, the adsorbate could be conveniently retained in a flow through reactor using externally applied magnetic field. Retention efficiency increased with increasing particle. Such changes were also influenced by the extent of loading GAC with MIO.

The studies and results presented in the thesis point to a new direction in the use of activated carbon. These include studies on Influence of the method of preparation of MIO-GAC on the distribution of iron oxide phases, modification of pore size distribution and their bearing on adsorption properties. Adsorption of volatile organic compounds from gas streams onto MIO-GAC. Design and evaluation of devices for MIO-GAC adsorption, retention in magnetic field and regeneration of the used adsorbent.

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