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A DOE Study of Ultrasound Intensified Removal of Phenol

P. R. Rahul, A. Kannan

***Abstract*—**Ultrasound-aided adsorption of phenol by Granular Activated Carbon (GAC) was investigated at different frequencies ranging from 35 kHz, 58 kHz, and 192 kHz. Other factors influencing adsorption such as Adsorbent dosage (g/L), the initial concentration of the phenol solution (ppm) and RPM was also considered along with the frequency variable. However, this study involved calorimetric measurements which helped is determining the effect of frequency on the % removal of phenol from the power dissipated to the system was normalized. It was found that low frequency (35 kHz) cavitation effects had a profound influence on the % removal of phenol per unit power. This study also had cavitation mapping of the ultrasonic baths, and it showed that the effect of cavitation on the adsorption system is irrespective of the position of the vessel. Hence, the vessel was placed at the center of the bath. In this study, novel temperature control and monitoring system to make sure that the system is under proper condition while operations. From the BET studies, it was found that there was only 5% increase in the surface area and hence it was concluded that ultrasound doesn't profoundly alter the equilibrium value of the adsorption system. DOE studies indicated that adsorbent dosage has a higher influence on the % removal in comparison with other factors.

***Keywords*—**Ultrasound, adsorption, granulated activated carbon, phenol.

I. Introduction

ADSORPTION is a phase transfer process in which certain component(s) of a gas, or liquid stream gets transferred to a contacting solid. Adsorbents such as Granular Activated Carbon (GAC) are effective mass separating agents because they are highly porous and have high surface area. The presence of phenol and its derivatives in aqueous solution lower water quality and threaten human health [1]. Industrial waste water sources of phenol include coal gasification and carbonization units, petroleum and petrochemical plants, plastics, etc. Phenol is toxic even at low concentrations, carcinogenic and in addition causes bad taste and odor [2]-[4]. According to EPA, permissible limits of phenol in waste water streams are less than 0.1ppm [4] Several methods such as adsorption, electrochemical oxidation, chemical coagulation, solvent extraction and membrane separation are available for removal of phenol from aqueous solutions [5].

The advantages of using ultrasound in solid-liquid mass transfer applications include more effective mixing and micro-mixing and faster mass transfer rates. In adsorption applications, it is not immediately clear whether the ultrasound will actually aid or hinder the rates of adsorption. There have been numerous studies on adsorption of phenol, and it has been reviewed that numerous factors play a role in influencing adsorption on activated carbon.

The most, frequently studied, basic parameters are adsorbent dosage (g/L), the initial concentration of the phenol solution (ppm), pH of the adsorbate solution [5]. studied the simultaneous adsorption of phenol and resorcinol onto GAC using simulated aqueous solution and has seen the effect of basic parameters. He has concluded that with increasing adsorbent dosage the % removal increased and it was the opposite in the case of initial concentration of the adsorbate solution, which showed a decrease in % removal with an increase in C_o (ppm). Moreover, it was found that acidic conditions of the adsorbate solution increased the % removal compared to higher pH values.

Very few who have studied the ultrasound-assisted adsorption of phenol have stated some important conclusions. Juang et al. [6] have stated that application of ultrasound decreases adsorption capacity of the adsorbent, but there is an increase in initial adsorption kinetics. Hamdaoui et al. [7] concluded that adsorption capacity, q (mg/g) of the adsorbent decreased with increasing power intensity of the ultrasound field in a p-chloro-phenol system. Breitbach and Bathen [8] have investigated the adsorption kinetics of fructose on Amber lite CR1320 at 313 K using different power inputs of ultrasound of power 20W, 40W, and 73W at frequencies of 337 and 1158 kHz. Schueller and Yang [9] studied a phenol-activated carbon and phenol-Dowex resin in a batch adsorber system at 295K. With the application of ultrasound power of 60 W and 1 MHz frequency, it was shown that adsorption uptake rates of the resin and activated carbon decreased compared to mechanical stirring at 250rpm. Jian- Bing Ji et al. [10] working on geniposide-polystyrene resin at a frequency of 18 kHz concluded that the adsorption equilibrium constant decreases with increasing ultrasonic intensity, pulse duty ratio and with decreasing pulse period.

Further, the sensitive frequency effects may act in combination with other physicochemical factors such as temperature, pH, concentration, adsorbent loading per unit volume of the solution. It is not easy to delineate the individual contributions on the rates of adsorption and the adsorbent equilibrium capacity. Therefore, it is important to segregate the effects of the different factors and also to identify how they influence adsorption rates when the different factors act together. Therefore, the aim of this paper is to perform a detail

Dr. A. Kannan and F. Rahul.P.R is associated with the Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600 036, Tamilnadu, India, (e-mail: kannan@iitm.ac.in, rahulpodi@gmail.com).

statistical study on the adsorption system by considering the factors such as Adsorbent Dosage (g/L), Initial Concentration (ppm), RPM and Machine (mechanical stirrer and ultrasonic baths).

II. Materials and Methods

A. Phenol

Phenol was procured from Merck India Pvt. Ltd. (Mumbai, India) and a stock solution of 1000ppm was prepared in a 1L standard flask. Solutions of required concentrations were prepared by suitably diluting the stock solution with distilled water. 250ppm, 500ppm, and 750ppm were some concentrations used for future experimental studies. Phenol procured was of Analytical Grade.

B. Granular Activated Carbon (GAC)

Granular Activated Carbon (GAC) was procured from Merck India Pvt.Ltd (Mumbai, India). These particles were thoroughly washed with distilled water using a mechanical stirrer. These particles were further filtered off from water and were dried in an oven at 700°C-800°C till there was no reduction in weight. These dried particles were kept in a desiccator so that the particles do not adsorb moisture and eventually affect adsorption capacity of the adsorbent particles.

C. Calibration of Uv-Vis Spectrophotometer

Uv-Vis spectrophotometer was chosen for the analysis of aqueous phenol sample to determine the concentration that is remaining in solution after adsorption had occurred onto the activated carbon. Calibration was done for Uv-Vis for different concentration of phenol, and the corresponding absorbance value was noted. Wavelength corresponding to phenol was found to be 269.5 nm, and it agrees with values reported in the literature [11].

D. Machines

Ultrasound machines (35 kHz, 58 kHz, and 192 kHz) were procured from Crest Ultrasonics, USA. It is well known that temperature of the water medium in the ultrasonic tanks increases with increase in time. Since adsorption required long operating time, novel temperature control measures were required to perform experiments accurately. The ultrasound machines mentioned above had rated the power of 250W (for 35 KHZ) and 500W (for 58 kHz and 192 kHz).

Apart from ultrasound assisted adsorption, conventional adsorption experiments were also planned which involved mechanical stirring experiments. In this study, mechanical stirring was chosen since it was found from preliminary experiments that it was better than orbital shaking experiments. In the case of mechanical stirring related experiments a Rashton turbine (impeller) was employed and it was connected to a system which had a digital rpm controller.

E. Calorimetric Studies

Though, as mentioned before in Section II D, the rated power of the machines was 250W or 500W and the power dissipated by the adsorption system and to the water medium (9L), will be less, has to be determined to effectively evaluate the performance of the respective machines on the adsorption system. To determine the power dissipated, calorimetric experiments are carried out which involves determining the increase in temperature with respect to time over 10 min at regular intervals. K-type thermocouples were used to monitor the temperature of the bath and the system for each 30 s. The power was eventually determined using (1), given below:

$$\text{Power (W)} = mC_p \frac{dT}{dt} \quad (1)$$

where m is a mass of the medium under consideration (in kg); C_p is specific heat capacity of the medium (J/kgK); T is temperature (K), T is time (s).

F. Cavitation Mapping in Ultrasound Machines

It is known that the glass reactor vessel used as the adsorption system is placed in the ultrasound tank and its optimum position in the tank has to be determined. Optimum position is based on the criteria of occurrence of maximum cavitation events. The temperature of the water medium at a particular point is an indirect measure of the cavitation events at the same point. So, K- type thermocouples were placed at 8 random points to determine the temperature. However, out of the 8 points, a center point was also chosen. Center point was chosen initially because placing the vessel at the center was convenient in terms of handling the entire experimental setup.

G. BET Studies

Eight samples were chosen in this case, but the GAC has treated in the presence of water and not the phenol solution. Experiments carried out with phenol solution would have led to adsorption of phenol onto the GAC, and further analysis of these particles with BET would not give the actual surface area values since phenol which is present in GAC may hinder the adsorption of N_2 gas.

After performing the experiments, the particles were separated from water, and they were dried in an oven at 120°C until there was no reduction in weight. All the eight samples were analyzed in ASAP 2020 V4.01, Micrometrics (V4.01 H) in CSIR – Madras – NML Unit, Chennai, and Tamilnadu.

H. Adsorption of Phenol

Adsorption system which forms the core of the entire experimental setup consists of a glass reactor. This glass reactor is designed as a jacketed vessel since the temperature of the system has to be maintained at 30°C. The reactor was filled with adsorbate solution (200ml was used throughout the entire study) of desired concentration, and the pH of the adsorbate solution was adjusted to the desired value by adding drops of 1N HCl (in the case of acidic conditions) or 1N of NaOH (in the case of basic conditions). Adsorbent particles (GAC) of desired dosage levels were added to the adsorbate solution.

Furthermore, during the course of the experiment temperature of the system was continuously monitored by inserting a K-type thermocouple. The experiment was carried out till equilibrium was attained, samples were taken at

intermediate time intervals to obtain the kinetics of adsorption, and then the samples were analyzed using Uv-Vis Spectrophotometer.

I. Determination of Adsorption Capacity

Adsorbate solution was analyzed to obtain the final concentration (C_f) from which adsorption capacity, q (mg/g) was found using the formula (2) given below [11]:

$$\text{Adsorption Capacity, q (mg/g)} = \frac{(C_o - C_e)V}{w} \quad (2)$$

where C_o- Initial concentration of the phenol sample (ppm), C_f is a final concentration of the phenol sample (ppm), V is the volume of the adsorbate solution (L), w is mount of adsorbent (GAC) taken (g).

J. Experimental Design

From preliminary experiments four process parameters and their levels were decided. The process parameters are Adsorbent Dosage (g/L), Initial phenol concentration (ppm), RPM of the mechanical stirrer and machine. pH which influences the adsorption process was also studied and found to be influencing the adsorption process when it is in acidic ranges. So pH was maintained at acidic conditions throughout the entire process.

Adsorbent Dosage (g/L), Initial phenol concentration, RPM of the mechanical stirrer were quantitative variables, and the fourth variable machine (mechanical stirrer, 35 kHz machine, 58 kHz machine, 192 kHz machine) was a qualitative variable. Since there were three quantitative variables, a Box-Behnken design could be employed which has less number of runs. However, the only disadvantage of using a BBD is extreme points cannot be operated, which is not very much required in this case [12]. Hence, BBD was selected over other designs.

Design Expert 8.0.6, Stat-Ease was used to generate the design and to analyze the responses further. The runs were performed in a randomized fashion to minimize the effect of the systematic error. Responses that were considered are percentage removal of phenol and experimental adsorption capacity (q (mg/g)).

III. Results and Discussion

A. Size of GAC Particles

With three trials of sieve shaking measurements, the sauter mean diameter of the particle was estimated to be 0.71 mm. GAC particles were separated in two sizes, 0.65 mm and 0.925 mm and were stored separately to make sure that experiments were carried out with particles of same sizes. The size distribution is shown in the Fig. 1.

B. Calibration of UV-Vis Spectrophotometer

With a phenol stock solution of 1000 ppm, various concentration ranging from 50 ppm to 750 ppm were prepared by suitably diluting with distilled water. These phenol solutions were again diluted since high concentration would result in absorbance values greater than 2, which is not reliable and advisory. Now, the absorbance corresponding to all these concentrations was determined using Uv-Vis Spectrophotometer.

A graph (Fig. 2) was plotted against absorbance values (abscissa) and the corresponding concentration values (ordinate) to yield a straight line with the R^2 value of 0.9908. Three trials were performed to check for repeatability.

C. BET Studies

8 samples, as mentioned in Section II G, were analyzed, and it could be found from the Table I that as-received granular activated carbon had a lower BET surface area compared to the other treated samples. It is evident that the samples exposed to ultrasound conditions have shown a considerable increase in surface area (decrease in the size of the particles, which is possible with exposure to ultrasound due to cavitation events) which in turn increases the equilibrium value or adsorption capacity, q. This increased adsorption capacity value may be not the actual adsorption capacity value for the given set of condition, i.e.; the new adsorption capacity value is bloated due to the increase in surface area caused by cavitation events.

To clearly understand the extent to which ultrasound affects the adsorption capacity, BET is performed. Now from the below Table I, it could be seen that the highest deviation of BET surface area, among all the 8 samples, was 5% which was in the case of "Only 35 kHz" sample. The effect of this 5% increase in BET surface on the adsorption capacity would be negligible. So, it can be concluded that ultrasound doesn't profoundly influence adsorption capacity by particle breakage rather it is the same (only in accordance with the effect of surface area on adsorption capacity) as that of the conventional method.

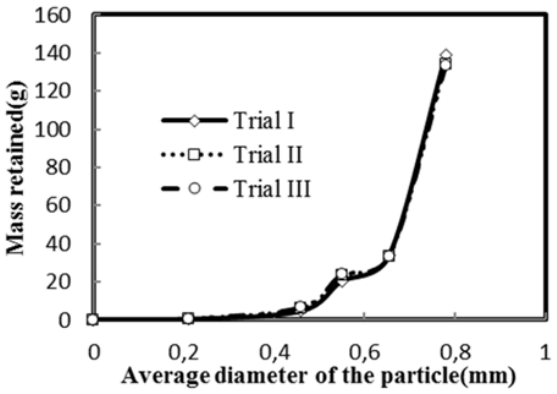

Fig. 1 Particle Size Distribution

D. Cavitation Mapping in Ultrasound Machines

K-type thermocouples were placed at 8 random positions to cover all the sections of the bath. Of these 8, one was placed deliberately at the center since it is easy to maintain the adsorption system at the center of the bath. It could be found from the below Figs. 2-7 that, with same initial temperature; there was no change in the temperature profile of all the 8 points.

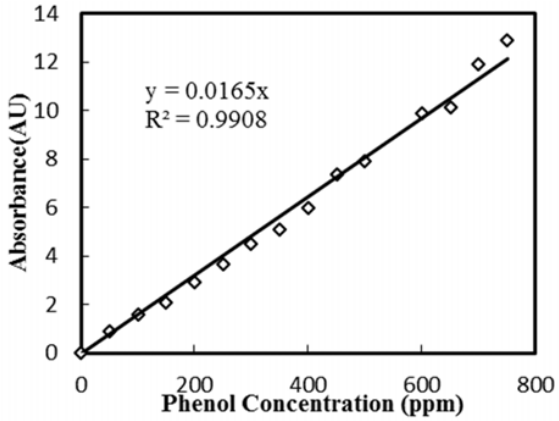

Fig. 2 Calibration of Uv-Vis Spectrophotometer

TABLE I
BET SURFACE AREA MEASUREMENTS OF 8 SAMPLES

S.No	Sample Name	BET Surface area (m^2/g)
1	Reference	876.892
2	Only 300 rpm	881.728
3	Only 35 kHz	926.765
4	Only 58 kHz	907.569
5	Only 192 kHz	881.378
6	35 kHz + 300 rpm	880.274
7	58 kHz + 300 rpm	896.532
8	192 kHz + 300 rpm	915.006

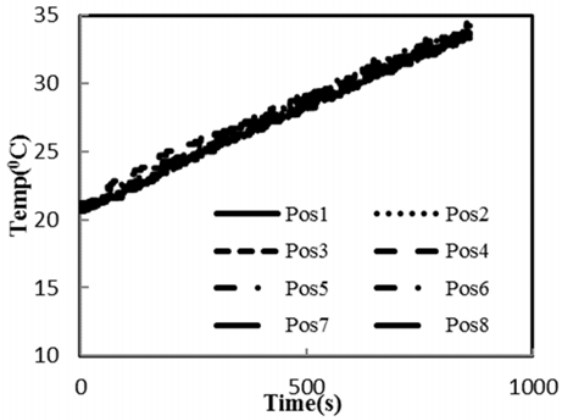

Fig. 3 Cavitation mapping at 8 positions in 58 kHz ultrasound machine

Two trials were performed to check for repeatability and all the ultrasound machines exhibited the same behavior. Figs. 3-5 indicate that the cavitation events are the same throughout the bath and hence the adsorption system could be placed anywhere.

In this study, the adsorption system was placed at the center since it was convenient in terms of handling the entire experimental setup

E. Calorimetric Studies

Calorimetric studies help us in determining the power input to the adsorption system and the ultrasound bath. In this case, the result pertaining to only 100% power setting is shown since all the experiments in the design matrix were carried out only at 100% power setting in all the ultrasound machines. Fig. 6 shows the variation of temperature in the adsorption system over 10min.

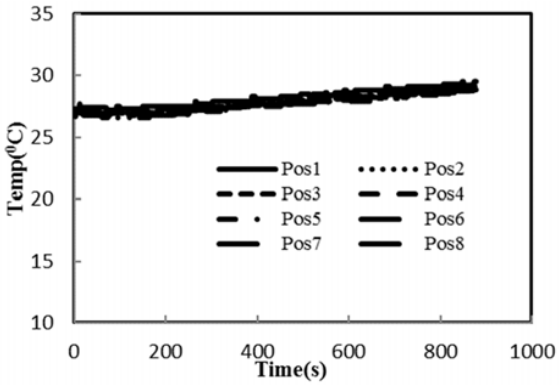

Fig. 4 Cavitation mapping at 8 positions in 35 kHz ultrasound machine

A straight line was fitted to the temperature profile of each individual machine, and the slope of the straight line was used to calculate the power received by the adsorption system when placed in that respective machine. The power was calculated using the formula mentioned in (1). It was found that the adsorption system was subjected to a power input of 2.1657 W in the case of 35 kHz machine, 3.342 W in 58 kHz machine and 3.1413 in 192 kHz machine.

These power values determined could help us in determining the energy required by the machines to attain equilibrium q (mg/g) and a comparison among the machines could also be done, consequently leading us to determine the effect of frequency on the adsorption process.

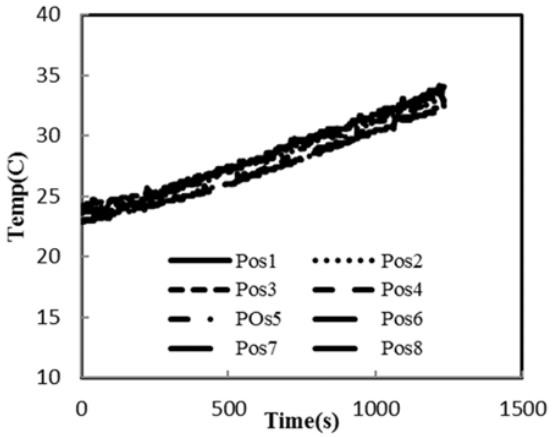

Fig. 5 Cavitation mapping at 8 positions in 192 kHz ultrasound machine

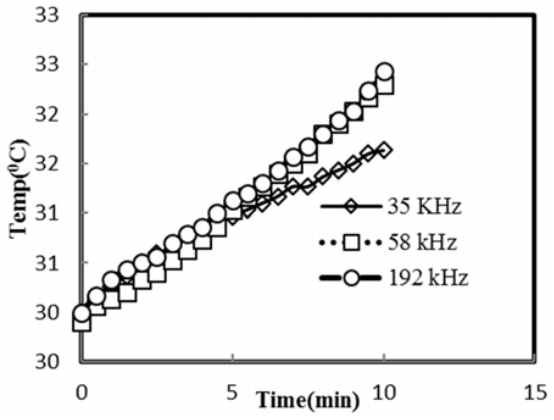

Fig. 6 Temperature profile of adsorption system in all three ultrasound machines (35 kHz, 58 kHz, and 192 kHz) at 100% power setting

F. Effect of Frequency on % Removal

Conditions involving only ultrasound were chosen for this analysis, i.e.; it was made sure that the selected conditions had rpm set to 0. It was done so to comprehensively figure out the effect of ultrasound (frequency and power) alone on % removal per unit power.

It could be seen from the Fig. 7 that at these 4 conditions 35 kHz machine had a significant effect on % removal per unit power compared to 58 kHz and 192 kHz machines. It is also to be noted that both 58 kHz and 192 kHz had almost the same effect in all the conditions and there was little change in the % removal per unit power value.

This conclusively says that frequency has an effect on % removal per unit power and it can be inferred that acoustic cavitation effects such as microstreaming, micro – jets and shockwaves associated with lower frequency (35 kHz) have a greater effect on % removal per unit power compared to acoustic streaming effects associated with intermediate or higher frequency (58 kHz and 192 kHz).

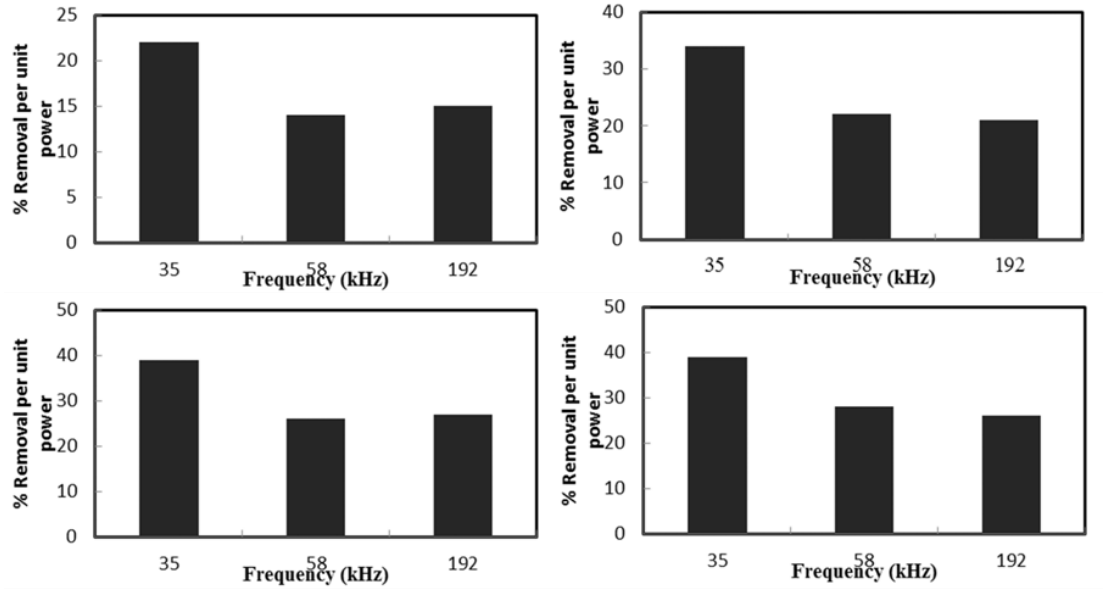

Fig. 7 Effect of frequency on percentage removal per unit power dissipated to the adsorption system.

IV. Conclusion

In this study, it was shown that other than conventional factors, certain other factors such as temperature control of the adsorption system, calorimetric measurements and cavitation mapping of the ultrasonic baths are required to obtain a conclusive result about % removal or adsorption capacity, q(mg/g). Moreover, it was concluded that low-frequency ultrasound aids in the removal of phenol compared to higher frequency ultrasound such as 58 kHz and 192 kHz. This concludes the fact that cavitation events such as micro-jets, shock waves associated with low-frequency ultrasound are more applicative in adsorption process rather than acoustic streaming effects associated with high-frequency ultrasound. With Design Expert there was a conclusive result on the influencing factors of the adsorption system. Importantly, with this model the interaction among the factors are accounted for along with the second order terms.

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