Sorption of Dyes using Cucurbituril

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Abstract

Cucurbituril was used as a sorbent for the removal of three dyestuffs, namely, Alizarin Red S, Basic Blue 41 and Ramazol Black B from aqueous solution. Equilibrium isotherms were constructed for all the three dyes used and from this the maximum sorption capacity for Alizarin Red S, and Ramazol Black B were found to be 22.8 mg g^{-1} and 21.7 mg g -1 respectively. Basic Blue 41 has much greater affinity for Cucurbituril with sorption capacity of 76.6 mg g^{-1}. The calculated intraparticle diffusion coefficient values for Basic Blue 41 are 0.307, 0.310, 0.318 and 0.322 mg/g min$^{0.5}$ for the initial dye concentration of 10, 20, 30 and 40 mg/L at 30. C Increase in temperature increased the sorption capacity. The values of ΔH for Basic Blue 41, Alizarin Red S and Ramazol Black B were found to be 10.7, 11.5 and 12.23 KJ respectively. It is found that increase in the content of potassium chloride increased the sorption process till it reached a limiting value particularly for the anionic dyes Alizarin Red S and Ramazol Black B.

**Keywords** – Cucurbituril, sorption, textile wastewater, sorption isotherms

INTRODUCTION

A dye may be defined as a substance, which when applied to the fabrics imparts a permanent color and the color is not removed by washing with water, soap or an exposure to the sunlight. [1] Textile industries use synthetic dyes extensively in the manufacturing process. [2-3] This practice results in the discharge of large quantities of aqueous coloured wastes into the environment. Many of these dyestuffs are inert and hence do not biodegrade. Many types of treatment procedures are available to remove the dyestuffs including biological methods, advanced oxidation process but adsorption process not only produces quality treated water but it is also cost effective. Cucurbituril has been suggested as sorbent for water treatment, namely for the

removal of aromatic compounds from the contaminated water sources and for the removal of dyes from textile wastewater. [4.]Sorption isotherms and contact-time experiments on specific solute/sorbent systems give the required scale up data for designing wastewater treatments systems which employ beds or columns of sorbents. The aim of the present work is to study the ability of Cucurbituril to adsorb/absorb three dyes, Alizarin Red S (ARS), Basic Blue 41 (BB) and Ramazol Black B (RB). These dyes were chosen for our study because they are not easily eliminated by biodegradation and sludge adsorption. .

Cucurbituril

Cucurbiturils are cyclic polymers of glycoluril. The name derives form the Latin for "pumpkin" due to the pumpkin shape of these molecules. Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) was rediscovered as a nonadecacyclic cage structure of hexagonal symmetry (Figure 1), which is readily assembled from urea, glyoxal and formaldehyde.[5] It has a relatively rigid structure with a hollow core of several picometers diameter which is accessible from the exterior. The substance dissolves readily in acidic aqueous solutions.

Several groups have synthesized different sized Cucurbit[n]uril using both unsubstituted and substituted glycouril. These new Cucurbit[n]urils have differing solubilites and cavity sizes; the larger ring sizes allow binding of larger guests. Cucurbiturils composed of 5, 6, 7, 8, and 10 repeat units have all been isolated, which have internal cavity volumes of 82, 164, 279, 479, and 870 $\overset{\circ}{A}^3$ respectively. It should be noted that there is no evidence of existence of Q[n] smaller than Q[5]. Cucurbit[10]uril is the largest analogue isolated so far.
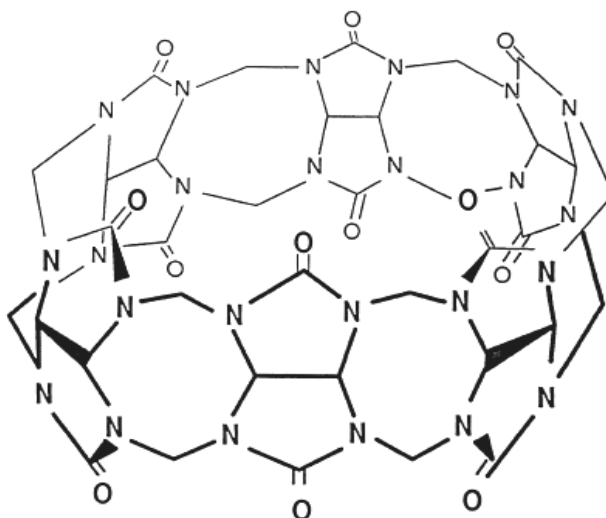
Figure 1: Molecular structure of cucurbituril[6]

Table 1 gives the dimensional parameters of cucurbituril(CB) homologues. From CB5 to CB8, the hollow cavity diameters increase from 4.4 to 8.8 Å and portal sizes increase from 2.4 to 6.9 Å. Larger cucurbituril homologues are able to bind larger guest molecules inside.[6, 7]

Table : 1 Dimensional parameter of CBn (n= 5-8).

	CB 5	CB6	CB7	CB8
Outer Diameter **a** (Å)	13.1	14.4	16.0	17.5
Inner cavity Size **b** (Å)	4.4	5.8	7.3	8.8
Portal size **c** (Å)	2.4	3.9	5.4	6.9
Height **d** (Å)	9.1	9.1	9.1	9.1
Cavity Volume (Å^3)	82	164	279	479

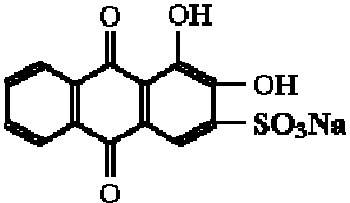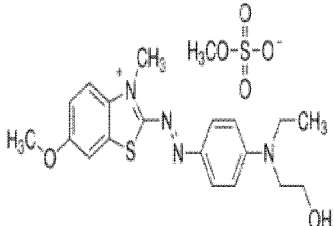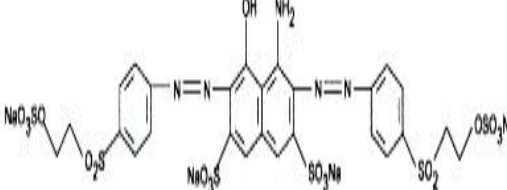**MATERIALS AND METHODS**
Glyoxal, urea, formaldehyde, concentrated hydrochloric acid were of analytical grade were used as such. Alizarin Red 'S' dye was obtained from E-Merck and the dyes Basic Blue 41 and Ramazol Black B were obtained from Sigma-Aldrich.

Sorbate:
The sorbates used in the present investigation and their structures are listed in Table – 2

Table -2 Structures of Sorbates

S.No	Commercial Name	Structure	λ_{max}	Supplier
1.	Alizarin red 'S'		540	E - Merck
2.	Basic Blue 41		617	Sigma-Aldrich

3.	Ramazol Black B		600	Sigma-Aldrich

pH of the Samples

pH of the samples was determined using a portable pH meter (Systronics Model). The pH meter was calibrated with 4.0 and 9.2 buffers.

Batch equilibration method

Stock solution of concentration 10^{-2} M of the dye solutions were prepared. From the stock solution various required concentration of the dye solution were prepared by dilution. 50mL of the dye solution was taken into a clean 250mL conical flask in which suitable amount of cucurbituril is added. The adsorption experiments were carried out in a batch process at a constant temperature. The known weight of adsorbent material was added to 50 mL of the

dye solutions with an initial concentration of 10 mg/L to 60 mg/L. The contents were shaken thoroughly using a mechanical shaker (Remi Model) rotating with a speed of 120 rpm. The solution was then filtered at preset time intervals and the residual dye concentration was measured by double beam UV-Visible spectrophotometer (Perkin – Elmer Model 550S) .

The wavelength was selected so as to obtain maximum absorbance for each dyestuff. The dyes used in this investigation obeyed the Beer – Lambert's law in the concentration range employed.

RESULTS AND DISCUSSION

Equilibrium Isotherms

The sorption capacity of Cucurbituril for various dyestuffs can be determined by measuring equilibrium isotherms. This is carried out by contacting 0.3 g of Cucurbituril with 0.05 dm^3 dye solution in sealed glass bottles placed in a constant agitator shaker bath. An equilibrium time of 5 days was allowed and at the end of the period the samples were filtered and their equilibrium concentrations were found by spectrophotmetric determination. The isotherms are shown in Figure 2. From the figure, it is clear that the maximum sorption capacity for ARS and RB were 22.8 mg g $^{-1}$ and 21.7 mg g -1 respectively. BB has much greater affinity for Cucurbituril with sorption capacity of 76.6 mg g $^{-1}$.

The surface of cucurbituril has many C=O groups and with possible polarization of this bond, , the surface in contact with water would be negatively charged. ARS and RB being acidic in nature, ionize in water to yield anionic coloured component. The approach of an acidic dye anion will suffer coulombic repulsion due to the presence of strong anionic groups in Cucurbituril. Basic Blue will ionize to give the

coloured cationic dye base and this will undergo strong attraction on approaching the anionic Cucurbituril structure. Therefore the sorption capacity increases.
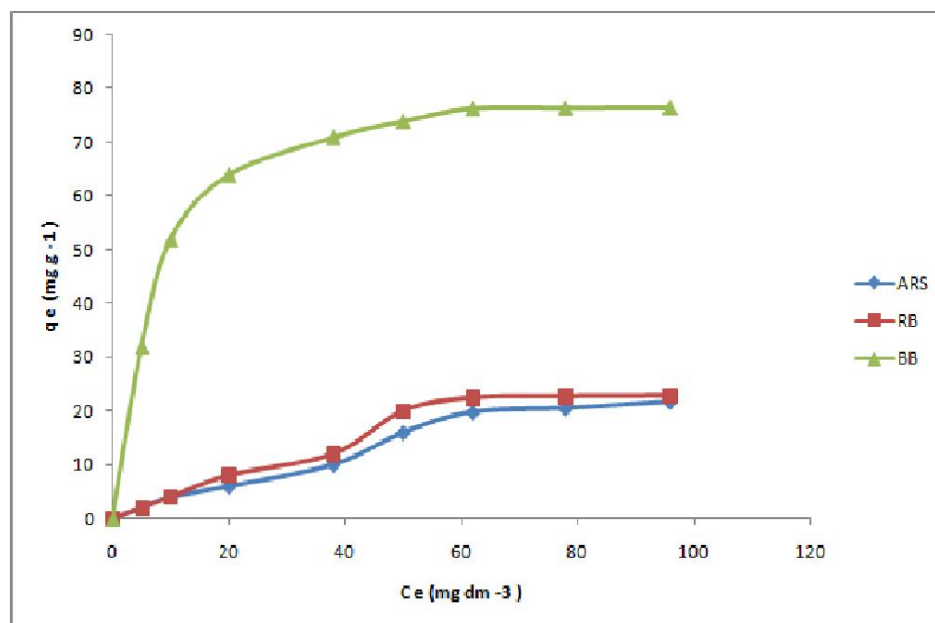

Figure :2 Sorption isotherms for dyes on Cucurbituril

Intraparticle diffusion

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies have shown [8-10] that the plot of Qt versus $t^{0.5}$ represents multi linearity, which characterizes the two or more steps involved in the sorption process. An intaparticle diffusion coefficient K_p is given by the equation:

$$K_p = Qt/t^{0.5} +C$$

Thus the Kp (mg/g $min^{0.5}$) value can be obtained from the slope of the plot of Qt(mg/g) versus $t^{0.5}$ for the dyes. For the dye BB, the sorption follows a two-phase process (Figure 3). The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion. The initial curved portion of the plot indicates a boundary layer effect while the second linear portion of the plot is due to intraparticle diffusion or pore diffusion. The slope of the second linear portion is due to intraparticle diffusion parameter K_p. The intercept of the pot reflects the boundary layer effect. The larger the intercept, the greater is the contribution of surface sorption in the rate limiting step. The calculated intraparticle diffusion coefficient values for BB are 0.307, 0.310, 0.318 and 0.322 mg/g $min^{0.5}$ for the initial dye concentration of 10, 20, 30 and 40 mg/L at 30. C.
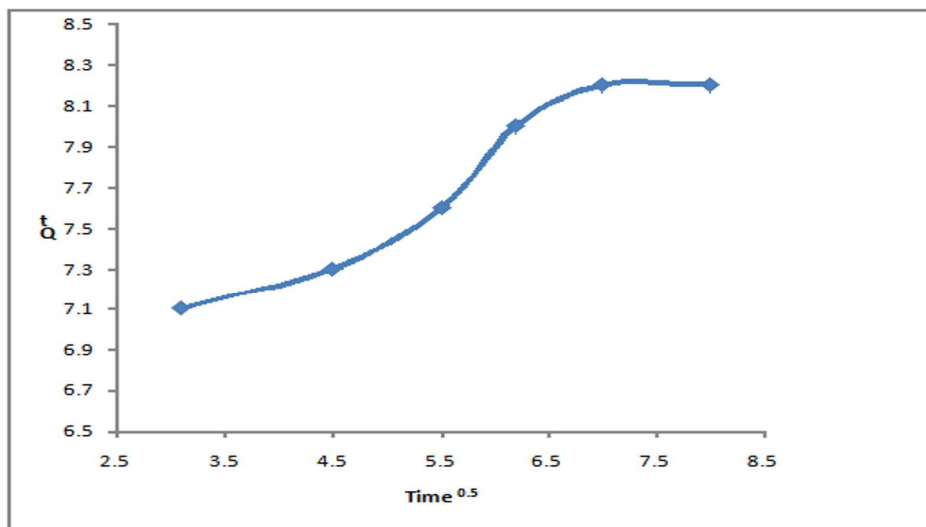
Figure : 3 Intraparticle diffusion effect for the removal of BB

Effect of Temperature
The effect of temperature on the sorption of BB and ARS are shown in Figs 4 and 5 respectively. As the temperature increases, the sorption capacity of RS increases from 22.8 mg g^{-1} at 20 .C to 26.3 mg g^{-1} at 60 C. For BB for same temperature range, the sorption capacity increases from 76.6 mg g^{-1} to 98.2 mg g^{-1} . Increasing the temperature would be increasing the mobility of large dye ion and hence there is increase in sorption capacity.
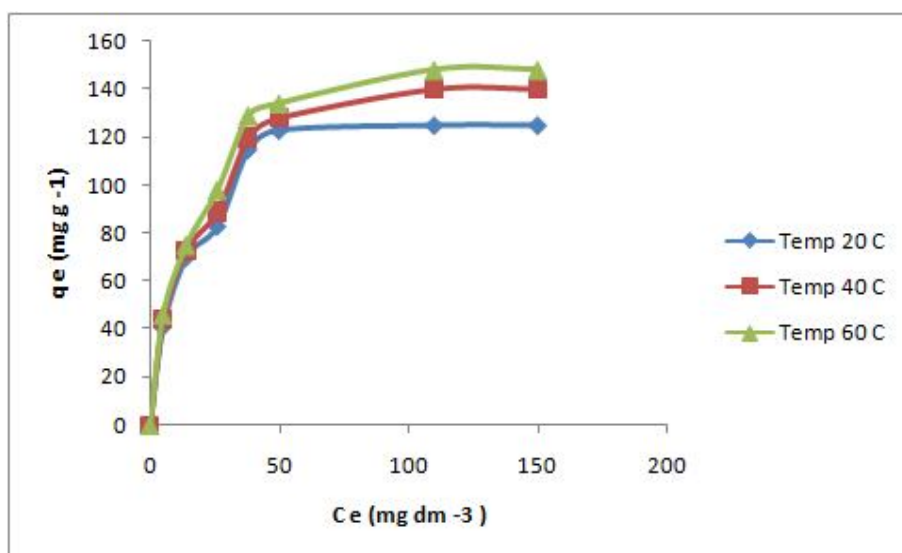
Figure : 4 Effect of Temperature on sorption of BB
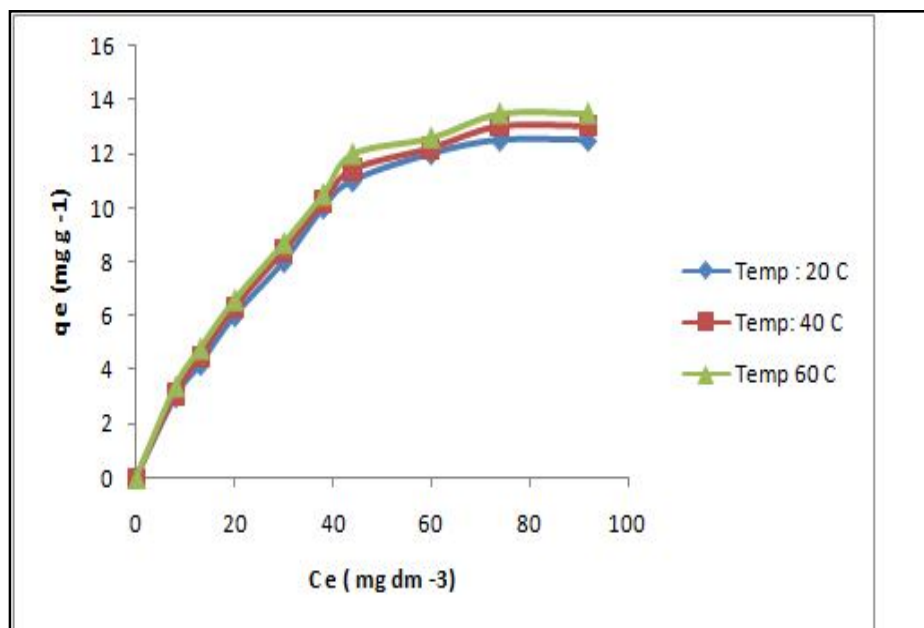
Figure : 5 Effect of Temperature on sorption of ARS

A number of equations exist enabling the distribution of dye between sorbent and the dye solution at equilibrium to be correlated.[11-13] Three widely used forms are Freundlich, Langmuir and Jossens which are represented by equations (1), (2) and (3) respectively.

$$q_e = K_F C_e^{1/n} \text{ ---} \tag{1}$$
$$q_e = K_L C_e / 1 + a_L C_e \text{ ----} \tag{2}$$
$$q_e = K_J C_e / 1 + a_J C_e^{\beta} \text{ ------} \tag{3}$$

In the present study sorption process is well accounted for by Langmuir equation. The linear form of the equation is given by (4)

$$C_e/q_e = 1/K_L + a_L/K_L . C_e \text{ ------} \tag{4}$$

The data for all the three dyes have been determined using the lest squares method and are tabulated in Table 3.

Table : 3 Langmuir constants for the sorption of dyes

Dye	Temperature .C	K_L $(dm^3 g^{-1})$	a_L $(dm^3 g^{-1})$	K_L/a_L $(mg\ g^{-1})$	r
BB	20	11.53	0.074	155.8	0.063
	40	14.86	0.093	159.8	0.051
	60	19.12	0.115	166.2	0.042
ARS	20	0.50	0.023	21.65	0.303
	40	0.65	0.029	22.41	0.256

	60	0.87	0.037	23.50	0.213
RB	20	1.10	0.048	22.81	0.172
	40	1.17	0.052	23.5	0.182
	60	1.21	0.061	24.4	0.193

The values K_L/a_L represent the maximum sorption capacity of cucurbituril for the dyes.

The constant K_L can be used to determine the enthalpy of sorption, ΔH, using the Clausius-Clapeyron equation (5)

$$K_L = Ac \exp(-\Delta H/RT) \text{----} \tag{5}$$

The values of ΔH for BB, ARS and RB were found to be 10.7, 11.5 and 12.23 KJ respectively. For a Langmuir type of sorption, the isotherm shape can be defined by a term r, a dimensionless constant separation factor. All the three dyes showed favourable sorption, that is, $0 < r < 1$.

Effect of Dye Concentration

The effect of dye concentration was studied by keeping the sorbent dose constant at 1 g. For sorption study, in the optimized period of contact time, the rate varies directly with concentration of sorbate. The activities of all the sorbent materials fall sharply with an increase in the initial concentration of dye. (Figure 6) It is well known fact that rate of exchange sorption is controlled by diffusion through a hydrostatic boundary layer called film diffusion control or through the pores of the region matrix called particle, diffusion control. The rate of exchange sorption is mainly controlled by film diffusion under the conditions of small particle, dilute solution and mild stirring and vice-versa in case of pore or particle diffusion.[14] More practically, both processes control it. The three distinct steps involves in the sorption of an organic/inorganic compound onto the pores of sorbent material are:

1. The sorbent molecules must be transferred from the bulk phase of the solution to the external surface of the sorbent particles is called as 'film diffusion'.
2. Transfer of sorbent molecules to an adsorption site on the inside of the sorbent particle is known as pore or 'particle diffusion'.
3. The sorbate particle must become attached to the interior surface of the adsorbent particle

that is 'sorbed'. In case of particles diffusion external transport > internal transportation and in film diffusion external transport < internal transportation and if external transportation is approximately equal to internal transportation, the transport of ions to the boundary may not be possible at significant rate.

In other words, at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low and subsequently the fractional sorption becomes independent of initial dye concentration. However, at high concentration, the available sites of sorption are fewer and hence the dye removal becomes dependent on initial concentration. However, at low concentrations, the initial uptake of dye is

rapid, indicting a rapid surface reaction. Thus the concentration of dye in an effluent will significantly affect the extent and rate of dye uptake by cucurbituril.
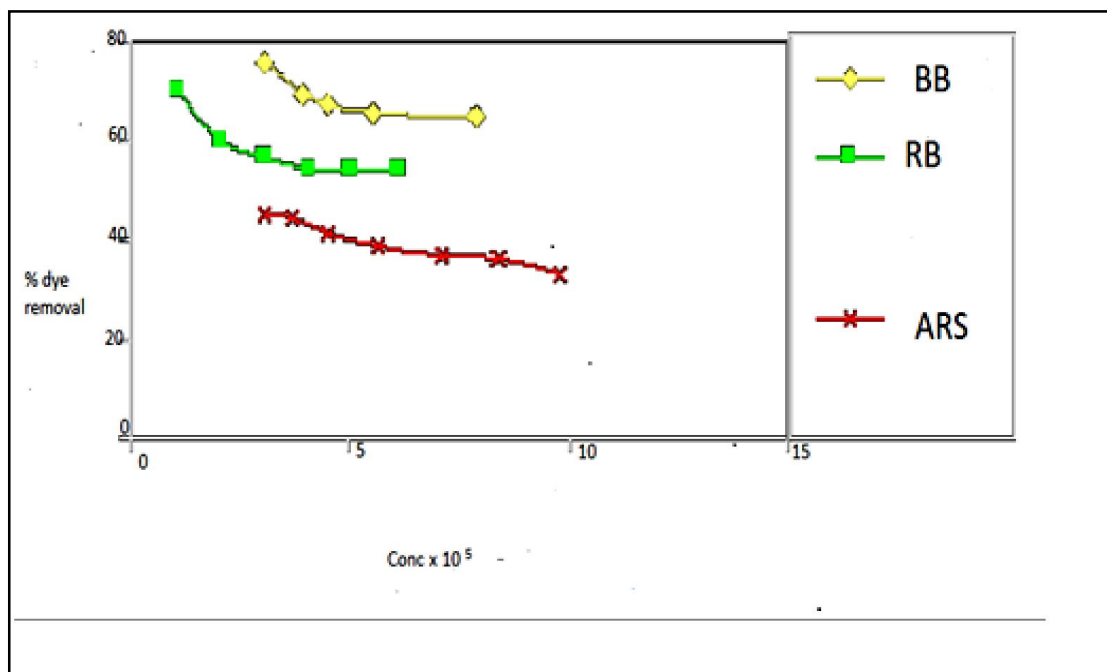
Figure: 6 Effect of Dye Concentration

Effect of pH

The pH of the solution is an important factor in controlling the process of sorption. The pH variation studies were conducted by changing the pH but keeping the other factors constant. The range varied from 2.0 to 9.0. The anionic dyes namely, ARS and RB showed a maximum adsorption at a pH of 5.0 and then a marginal decrease for the remaining range of pH. When the pH is low, it can increase the positive charge on the sorbent surface which can attract the negative functional groups located on the anionic dyes.

The effect of pH on the cationic dye BB showed a reverse trend. As the pH was increased, the sorption increased. The lower sorption of cationic dye in acidic pH is due to the presence of excess H^+ ions competing with the dye cation for the sorption of the dyes. The results are indicated in table 4.

Table : 4 Effect of pH on sorption of Dyes
[Dye] 40 mg/L Cucurbituril : 5 g Temperature : 30 C

S.No	pH	% Dye removal ARS	% Dye removal RB	% Dye removal BB
1	2	82	83	38
2	3	78	78	58

3	4	75	76	65
4	5	88	90	68
5	6	70	5	80
6	7	60	62	82
7	8	55	60	85
8	9	54	58	85

Effect of added salt

Potassium chloride was chosen as the salt to be added as most wastewaters contain these ions namely potassium and chloride. It is found that increase in the content of potassium chloride increased the sorption process till it reached a limiting value particularly for the anionic dyes ARS and RB. The availability of potassium ions would enable a higher neutralizing concentration of potassium ions on the surface of cucurbiuril compressing the electrical double layer. This makes it possible for ARS and RB anions to approach the surface more closely and become available for more intense surface adsorption**.**

Conclusion

The present work involves the study of sorption process of three dyes, Alizarin Red S, Basic Blue and Ramzol Balck B using a synthesized sorbing material Cucurbituril. The macrocyclic compound Cucurbituril was synthesized as per the procedure in the literature and the product was characterized.

In order to identify the mechanism involved in the sorption process, the experimental data was fit into an intraparticle diffusion plot. Langmuir type of sorption was found to be most suitable isotherm. All the three dyes showed favourable sorption, that is, $0 < r < 1$. In the optimized period of contact time, the rate varied directly with concentration of sorbate. The anionic dyes namely, ARS and RB showed a maximum adsorption at a pH of 5.0 and then a marginal decrease for the remaining range of pH. The effect of pH on the cationic dye BB showed a reverse trend. As the pH was increased, the sorption increased.

Thus the possibilities of using cucurbituril as a sorbent for the treatment of industrial wastewater can be explored in future.

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