

Potential Adsorption of Crystal Violet from Waste Water by Azadirachta Indica (Neem) Leaf Derived Carbon

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Abstract—As a sequel to the removal of waste using wastes-based technologies, we present here our results of the study utilizing neem leaf, an agricultural waste, as an interesting carbon precursor for Crystal Violet (CV) dye removal. Waste neem leaf is activated to form an activated carbon and it is tested for its efficiency by the adsorption studies. Dye solution of CV was prepared and tested for its removal efficiency with this activated carbon. The Batch mode of experiments has been carried out for adsorption studies of the Azadirachta indica (Neem) Leaf Carbon (NLC). Effect of parameter like pH, adsorbent dose, contact time, temperature and initial metal ion concentration were also determined. The optimum conditions obtained were 60 min contact time, 1.0g adsorbent dose, 40 °C, 100mg/L CV and pH 12 for CV removal. The results revealed that CV dye is considerably adsorbed on neem leaf derived carbon and it could be economic method for the removal of CV from aqueous solutions. Moreover, this study gives a value-added utilization of biomass to remove CV from waste water. The results revealed that NLC adsorbent is potentially low-cost adsorbent for the removal of dye.

Index Terms—Adsorption, Bioadsorbent, Biomass Carbon, crystal violet, neem Leaf

I. INTRODUCTION

One of the environmental issues worldwide is the contamination of water resources by industrial effluents. Among various industries, the textile industry waste water is considered to be an intensive water consuming area of activity besides utilizing a wide variety of chemicals and dyes. The effluent discharged from the textile industries leads to grave concern for the environment and health if it is to be mixed with sewage system or neighboring water-receiving bodies. Effluent is a complex solution of chemicals having intense colour value besides salt in terms of high TDS. Although the textile dyes

contribute only a small portion of the total volume of discharged wastewater after the dyeing process, they are deeply coloured (Gandhirajan & Selvi 2002). Colour removal is generally considered more important than the removal of the soluble colourless chemical contaminants since it is an aesthetic problem and also detrimental to microbial life. The coloured wastewater interferes with the photosynthetic activity of plants impeding solar radiation penetration and thereby affects the ecosystem. Conventional wastewater treatment processes do not remove the dyes and colours as they are fairly stable to light, heat and resist biodegradation because of their complex molecular structures.

In recent years a number of processes such as physical, chemical and biological (e.g., Adsorption, coagulation/flocculation, biodegradation, ion-exchange, chemical oxidation, ozonation, reverse osmosis, membrane filtration and electrochemical methods) have been subjected to remove dye molecules from effluents (Blackburn 2004; Crini 2007). However, it is evident from the literature that the ambiguity of applicability and shake the flask status of biological processes, limits of chemical coagulation / flocculation to produce good quality effluent besides sludge handling problems. Moreover, economical non-feasibility and possible detrimental effects of chemical oxidation along with technical and economic constraints of reverse osmosis due to the short membrane life make adsorption a more attractive alternative method for the wastewater treatment. Adsorption using activated carbon has been conventionally practiced for the treatment of coloured wastewaters. However, the prohibitive cost of activated carbon has restricted its use and hence it is desired to replace it by low cost effective and easily available alternatives.

Activated carbon in granular and powdered form is the most widely used material as an adsorbent. However, it has the disadvantage of being quite expensive depending on the quality. Both chemical and thermal regeneration of spent carbon is expensive, impractical on a large-scale and produces additional effluent and results in considerable loss of the adsorbent. This has led many workers to search for the use of cheap and efficient alternative materials (Aksu 2005).

Performance of non-conventional adsorbents for wastewater treatment has been used by various workers as has been referred (Singh & Srivastava 2001). Chemically treated Psidium guava leaves and Neem saw dust have been used to the adsorbate like methylene blue, malachite green, crystal violet and Rhodamine-B. Chitin, cellulose derivatives and chitosan have been used for treatment of dyestuffs, acid dyes and basic dyes. Activated alumina, clay, waste Fe(III) / Cr(III) hydroxides, carbonized wool, silica, chemically treated modified peat have been extensively used for the treatment of dyes. Fly ash and boiler bottom ash is treated as an adsorbent for methylene blue and malachite green and also victoria blue. Paddy straw is also used for congo red. Palm fruit bunch is used as an adsorbent for basic red and basic yellow. Rice husk carbons for safranine methylene blue and perlite for methylene blue are some of the adsorbents used for treatment purposes. Eucalyptus bark also used for treatment of reactive dyes. Bentonites are used for treatment of acid yellow-23, direct red, basic violet-10 and basic oxygen furnace slag for acid black-1. Ashes of cow dung, saphada, rice husk, bagasse and bottom ash are the adsorbent for the reactive yellow-85, reactive red-31, acid violet-49 and reactive blue-5. Although these adsorbents have been used considering their cost effectiveness and availability, wide variations in the quality and localized availability resulting in higher transportation cost naturally restricts their prospect for industrial utilization (Singh & Srivastava 2001).

Now turning to the global tendency with regard to the use of plant wastes and agro-industrial wastes, conversion of these into carbon may add economic value to a large quantity of wastes that are generally discarded. In India, annual production of biomass waste is estimated to be 135 thousand metric tons mostly from agriculture residues, industrial, domestic and yard wastes (India Solid Waste Management, 2014). With the view of utilizing waste, we have

chosen the biomass viz., banyan tree leaf and it is important to look how these wastes are really taken and how it could be transformed/utilized in a better way with a concern on society.

Thus it is clear that these waste biomass materials might have only little or no economic value and may often present disposal problems by and large. But there is wise possibility left to us in converting these low-cost biomass materials into activated carbon, which would add economic value, help reduce the cost of wastes disposal and most importantly provide a potentially inexpensive alternative to the existing high-cost commercial activated carbon powders. It is a freely and abundantly available local resource and it can be used for the preparation of an effective activated carbon and for its application in the textile wastewater treatment.

Thus, the present work would represent an essential and innovative attempt to produce carbon powders from biomass waste by thermal treatment that may have industrial applications as adsorption of removal of crystal violet dye. The adsorption study of dye from waste water was done by varying pH, initial concentration of dyes, adsorbent dosage, temperature and contact time and the results are presented in systematic way.

II. EXPERIMENTAL

2.1 Preparation of Neem leaf Carbon (NLC)

The biomass precursors were washed with distilled water, dried in shade and thermally treated in a furnace at 350⁰ C for 2 hours, furnace cooled to give a black mass. The black mass from the furnace was collected, and washed with dilute HCl and de-ionized water until the pH of the decant solution was approximately 7. The char was dried at 80⁰C in oven, ground using mortar and pestle and finally sieved to uniform size for 250-micron particles. The above obtained powder is called Neem leaf Carbon (NLC) and used for further studies.

2.2 Stock solution preparation

Stock solution of crystal violet dye is prepared dissolving 100mg/L of crystal violet in 1litre of water. Hydrochloric acid and sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies. The adsorption studies were done in 250 ml Erlenmeyer flasks with

100 ml volume of CV solution. It was Shaked on a rotary shaker set at 120 rpm speed and at room temperature. The supernatant liquid was collected and analyzed for remaining dye concentration using UV spectrophotometer and the % removal of dye was calculated.

The amount of dye adsorbed per gram of the biomass was calculated using the equation:

$$q_e = (C_i - C_e)V/M$$

where q_e is the amount of dye biosorbed per gram of the biomass in mg/g, C_i is the initial concentration of the metal ion in mg/L, C_e is the equilibrium concentration of the dye in mg/L, M is the mass of the biomass in grams and V is the volume of the metal ion in litres. The experiment was done in triplicate and the mean value was taken for each parameter.

III. RESULTS AND DISCUSSION

3.1 Effect of Contact Time on Dye Adsorption

The effect of contact time on the adsorption of crystal violet dye using NLC was studied and the results are tabulated in Table 1. All parameters such as dose of adsorbent, temperature, initial dye concentration and pH of solution were kept constant.

Table 1 Effect of contact time on crystal violet dye adsorption [CV dye]-100mg/L, pH-7, Wt of biomass carbon – 0.5g, Temp -30 °C

Time (min)	% removal of crystal violet
10	30.6
20	41.7
30	50.3
40	60.7
50	65.5
60	92.2
70	92.2
80	92.2

From the results, it is noted that % of dye removal increases with increase in contact time before equilibrium was reached, after which there was no significance increase in dye adsorption uptake. This is because the strong chemical binding of the adsorbate with adsorbent requires longer contact time for the attainment of equilibrium. Available adsorbent studies

in the literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are difficult to occupy due to repulsive forces between the solute molecules on the solid and bulk phases.

From table 1, it can be seen that the rate of adsorption is very rapid at initial period of contact time. Thereafter, it decreased gradually with time until adsorption is reached at the equilibrium point. This trend of adsorption kinetics is due to the adsorption of dye on the exterior surface of adsorbent at the initial period of contact time. When the adsorption on the exterior surface reached saturation point, the dye diffused into the pores of the adsorbent and is absorbed by the interior surface of the adsorbent. The curves of contact time are single, smooth and continuous leading to saturation. These curves indicate the possible monolayer coverage of dye on the surface of NLC (Dogan & Alkan 2003; Inbraj & Sulochana 2002; Malik 2003; Wong & Yu 1999). The equilibrium time for NLC -CV is 60 min, thereafter, no further adsorption occurred with prolonged time.

3.2 Effect of Ph On Dye Adsorption

The effect of pH on the adsorption of CV using NLC was studied and the results are tabulated in Table 2.

Table 2 Effect of pH on dye adsorption [CV]-100mg/L, Time-60min, Wt of biomass carbon-0.5g, Temp- 30 C

pH	% removal of CV
2	89.7
4	90.8
6	92.9
8	97.0
10	97.5
12	97.8

The value of pH is known as one of the most important factors in considering the removal of dye molecules from aqueous solutions. To determine the optimum pH conditions for the adsorption of cationic dyes onto NLC, the effect of pH is studied over a wide pH range of 2-12. The results infer the effect of pH on the adsorption quantity of various cationic dye namely

CV. It can be seen that dye adsorption is unfavorable at $\text{pH} < 4$. The decrease in the adsorption with a decrease in pH may be attributed to two reasons. As the pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye cations due to electrostatic repulsion (Batzias & Sidiras et al 2007) while, the lower adsorption of dyes at acidic pH is due to the presence of the excess H^+ ions competing with dye cations for the adsorption sites of mesoporous carbon. It is known that pH can affect the structural stability of dyes and consequently its colour intensity (Sun & Tomkinson 2001). It may be due to the structural changes of dye molecules at high pH. On the contrast, the surface of the NLC acquires a negative charge at a high pH, OH^- on the surface of the adsorbent favours the adsorption of cationic dye molecules. The electrostatic attraction between the negatively charged surface of the NLC and cationic dye molecule could result in an increase in the adsorption capacity of various dyes. Several investigations reported that the adsorption quantity of cationic dyes usually increased as the pH increased (Janos 2003; Singh et al 2003). Therefore, from the results of the experiment and the point of view of application, pH above 7 is chosen as the appropriate value of the initial solution.

Differences in % removal ranged from 91.7 to 97.8 % and increased with the pH for NLC-CV .

3.3 Effect Of Adsorbent Dose on Dye Adsorption

The effect of adsorbent dose on the adsorption of dye using NLC for a given initial concentration of the adsorbate was studied and the results are tabulated in Table 3. The parameters namely, pH, contact time, and temperature are kept constant.

Table 3 Effect of adsorbent dose on dye adsorption [CV]-100mg/L, Time – 60min, pH – 7, Temp – 30 °C

Wt of biomass carbon(g)	% removal of CV
0.2	60.3
0.4	77.0
0.6	91.6
0.8	92.0
1.0	92.1
1.2	92.1

It clearly indicates that the dye removal increased with increase in adsorbent dosage and it is evident that the removal of dyes increased from 60.3 to 92.1 % with respect to CV system. As the adsorbent dosage increased from 0.2 to 1.2 g with respect to the fixed dye concentration, 100 mg/L. This is because of fixed initial dye concentration, increase in the total adsorbent dosage provides a greater surface area or active sites thus it increases the adsorption potential. However, it is observed that after the higher % removal of dyes, there is no significant change in the percentage removal of dyes. It may due to overlapping of active sites at higher adsorbent doses. So, there is no appreciable increase in the adsorptions because of saturation of the effective surface area and the results a conglomeration of exchange particles (Patil et al 2011).

The optimum dosage of adsorbent is 0.8 g for NLC-CV systems. Similar trends are reported with Methylene blue onto beer brewery waste (Tsai et al 2006), Cationic dye adsorption on peanut hull (Gong et al 2005), Basic dye onto banana stalk waste (Hameed et al 2008), Kapok hull onto Malachite green (Syed Shabudeen 2011).

3.4 Effect Of Temperature on Dye Adsorption

The effect of temperature on removal of dye using NLC was studied within the range of 25 to 50 °C and the results are tabulated in Table 4. Other parameters such as dose of adsorbent, pH, metal ion concentration, contact time and pH of solution were kept constant.

Table 4 Effect of temperature on dye adsorption Wt of biomass carbon – 0.5g, Time – 50min, pH – 7, [CV]-100mg/L

Temperature (°C)	% removal of CV
25	87.2
30	90.8
35	94.6
40	96.3
45	90.8
50	86.5

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The temperature showed the positive and then negative effect on adsorption of dye using NLC. With increase

in temperature the removal of dyes was increased from 87.2 to 96.3% for CV after that increase in temperature leads to desorption of dyes.

From the results it is clear that the low temperature is in favor of dye removal. This may be due to a tendency for the dye to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of dye is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This implies that the adsorption process was exothermic in nature. Similar findings are also reported by other researchers (Chakraborty et al 2011).

3.5 Effect of Initial Metal Ion Concentration on Dye Adsorption

The effect of initial dye concentration on the adsorption rate was studied in the range of 100mg/L to 300mg/L (variation of 50mg/L) at pH 7, temperature 30 °C, 0.5g of adsorbent and 60/70 min contact time. The results obtained are tabulated in Table 5.

Table 5 Effect of initial dye concentration on adsorption Wt of biomass carbon – 0.5g, Time- 60min, pH-7, Temp-30 °C

[CV](mg/L)	% removal of CV
50	92.1
100	90.3
150	88.1
200	77.5
250	64.3
300	45.2

It is evident from the result that, as the concentration of dyes are increased, there is a decrease in % removal. It is because, the initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of dye molecules between the aqueous phase and the solid phase resulting in higher probability of collision between adsorbent and the active sites (Zou et al 2011). The increase in initial dye concentration also enhances the interaction between dye molecules and NLC i.e. adsorbent. Therefore, an increase in the initial concentration of dye enhances the adsorption uptake of dye and results in higher adsorption, while the adsorption is carried out for a fixed number of active sites, there is a decrease in the

% removal of dye. This may originate from the microporous structure of the fabricated activated carbon. It is important to note that micropores are often the major contribution to the adsorption capacity, but the adsorbate molecule should be small enough to penetrate into the micropores (Mohammadi et al 2010). Hence a higher initial dye concentration will enhance the adsorption process. The dye removal decreased from 92.1 to 45.2% for NLC-CV system as the dye concentration is increased from 50 to 300 mg/L. Similar results have been reported in the literature on the extent of removal of dyes (Deo & Ali 1993; Arivoli et al 2011).

IV. CONCLUSION

The agricultural waste products are predominant in the commercial agricultural practicing country like India, where the effluent holding the toxic pollutant from waste water is a threatening factor. The low-cost effective adsorbents from the agricultural waste for the quantitative removal of cationic dyes from aqueous solution are imperative. This study envisaged the equilibrium and the dynamics of the adsorption of various cationic dyes namely, crystal violet onto this carbon prepared by Neem leaf.

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