Removal and Recovery of Direct Red 81 Dye using Argemone Mexicana: Column Studies

Shraddha Khamparia, [1,*] Dipika Jaspal[2]

[1]Symbiosis Institute of Research and Innovation, Symbiosis International University, Gram Lavale, Tal.Mulshi Pune-412115, (Maharashtra) India. shraddha.khamparia@sitpune.edu.in

[2]Symbiosis Institute of Technology, Symbiosis International University, Gram Lavale, Tal.Mulshi Pune-412115, (Maharashtra) India. dipikaj@sitpune.edu.in

*Corresponding Author Email: shraddha.khamparia@sitpune.edu.in

Abstract

Argemone Mexicana, a crop weed, was utilized as a prospective adsorbent for removal and recovery of Direct red 81, a water soluble textile dye. The dynamic removal of the toxic dye by the natural adsorbent was studied in a fixed bed column. By percolating the dye solution through prepared fixed-bed columns of the adsorbent, bulk removal of the Direct red 81 was carried out and necessary parameters such as time involved in establishing the primary adsorption zone (t_x), time required by primary adsorption zone to move down its length length (t_δ), time of initial formation of primary adsorption zone (t_f), fractional capacity of the column (f), mass rate flow of the adsorbent (F_m) were determined in order to evaluate the saturation factor. Argemone Mexicana seeds adsorbed 3.66 mg from 13.512 mg of the dye solution at neutral pH. Percentage recovery of 83.03% of the dye was obtained with 98.33% saturation of the bed column. Results suggested Argemone Mexicana to be a potential adsorbent for removal of Direct red 81 dye from its aqueous solution. Consequently, column adsorption and desorption experiments confirmed the practical applicability of the present research.

Key words: Adsorption, Argemone Mexicana, Column Studies, Desorption, Direct red 81

1. Introduction

Presence of synthetic dyes in aquatic environment has been of great concern because of their adverse effects on flora and flora present in the environment. Large number of dyes are manufactured all over the globe and are consumed by different processing and

manufacturing industries [1, 2]. Being the prime consumers of synthetic dyes, textile industries becomes one of the major contributors to water pollution. Presence of azo linkages in these dyes makes them toxic and carcinogenic in nature [3-4]. Keeping in mind the scarcity of this valuable natural resource, there is an urgent need for treatment and reclamation of the effluents discharged from the textile industries.

Various physical, chemical and biological techniques have been employed for treatment of the colored effluent since decades, amongst which adsorption technique is widely used [5]. Several adsorbents have been explored for dye removal till date. Investigation of adsorption with activated carbon has been carried out by number of researchers [6-8]. The sustainable approach of utilization of natural materials during adsorption is one of the economic strategies followed in recent years for decolorization of colored effluents [9-11].

Direct red 81 which is a sulphonated di azo textile dye has been chosen for the study which is known for its carcinogenic nature and toxicity towards animals and humans [12-13]. Studies showed that a significant amount of dye intake results in gastro-intestinal discomfort producing nausea and vomiting. Present study deals with employment of a weed for removal of this textile dye through column adsorption. Argemone Mexicana, commonly known as Mexican prickly poppy is available all over the globe in barren lands and road sides [14]. The seeds are toxic in nature and used for adulteration purpose in India with mustard seeds [15]. The plant is harmful to the native crops [16].The investigation deals with the exploration of decolorizing property of the Argemone Mexicana seeds.

Both batch and column studies have been investigated for different adsorbents, but column studies provide a better practical approach toward dye removal. [17-19]. The present manuscript deals with the fixed bed column studies for the removal of Direct red 81 dye using Argemone Mexicana seeds.

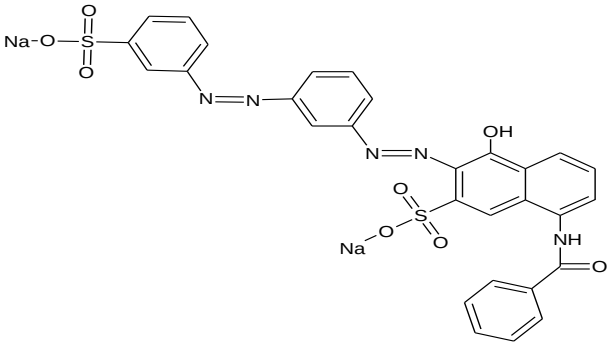
2. Experimental

2.1. Materials and Method

Direct red 81 is a sulphonated di azo dye having IUPAC name as disodium, (3E) -7-benzamido*4*oxo-3-[[4-[(4-sulfonatophenl) diazenyl] phenyl] hydrazinylidene] naphthalene-2-sulfonate. The dye was procured from Sigma- Aldrich. The structure and physiochemical properties are given in table 1. The stock solution of 10^{-3} M was prepared in distilled water. All working solutions were prepared by diluting the stock solution with

distilled water to the needed concentration. The concentration of the solutions during adsorption studies were evaluated using Double beam Spectrophotometer.

Table 1. Physiochemical properties of Direct red 81 dye

Parameters	Values
Molecular Weight	675.60 g/mol
Molecular Formula	$C_{29}H_{19}N_5Na_2O_8S_2$
Solubility	Soluble in water
Absorbance maxima	508 nm
Synonyms	Direct fast red 4B, Duasyn Direct red 8B and Pergasol red 2B.
Structure	
Nature	Anionic Acidic Dye

2.2. Preparation of adsorbent

Fresh seeds of Argemone Mexicana were collected from barren lands and road sides of Lavale village, Pune City, India. The seed pods were dried in sunlight and were taken out from the pods. The seeds were then washed with distilled water to remove impurities. The seeds were dried in sun for 24 hours and in oven for four hours at 110 °C. The sundried seeds were then grinded to get a fine powder and sieved to get a particle size ranging from 425-300 µm using IS: 460 BIS sieve. The powdered and sieved Argemone Mexicana seeds were then submerged in water for 12 hours to get the slurry which was to be fed into the column.

2.3. Selection of Eluent

Selection of the eluent is important to obtain the breakthrough capacity of the column. Various solvents were examined to get the suitable eluent for the desorption study. Sodium hydroxide, Di ethyl ether, Hydrochloric acid, Ethylene diamine tetra acetic acid, Acetone, Methyl alcohol and formaldehyde were tested for the removal of adsorbed dye from Argemone Mexicana seeds. The experimentation indicated best results with 1 N NaOH. Hence for desorption studies, 1 N NaOH was chosen as a suitable eluent.

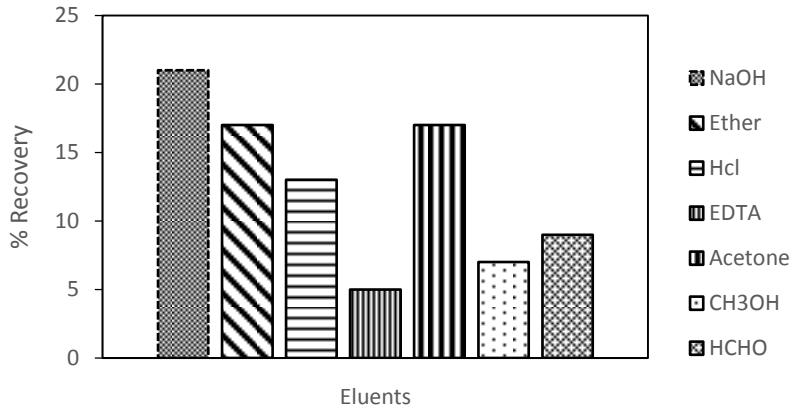


Figure 1. **Percentage recovery of Direct red 81 dye from Argemone Mexicana seeds by different eluents**

2.4. Column Studies

A glass column of 1 cm internal diameter and 30 cm length was taken. The glass column was filled with 1.5 g of Argemone Mexicana seeds which was supported on glass wool. To avoid the air entrapment in the column, adsorbent was fed into the glass column in the form of slurry. The flow rate was varied from 0.2 ml/min to 0.5 ml/min to achieve maximum removal of Direct red 81 and it was found that maximum uptake was achieved at 0.33 ml/min. The flow rate of the column was therefore maintained at 0.33 ml/min to achieve maximum decolorization. Direct red 81 dye solution of 10^{-4} M concentration was percolated through the column while maintaining the flow rate (0.33 ml/min) at room temperature (28±2°C). The pH of the dye solution was maintained at 7.0. Every 10 ml of effluent was collected analysed spectrophotometrically to gain the concentration. Column studies were terminated when the column was exhausted i.e., when the concentration of effluent became equal to the dye concentration percolated from the top of the column. On the basis of collected aliquotes a graph between volume and concentration of effluent was plotted, to get the desired parameters.

After complete exhaustion of the column capacity, desorption studies were carried out with a flow rate of 0.33 ml/min using 1N NaOH solution. The method adopted for the fixed-bed column study was as described by Weber [20]. Parameters such as length of primary ad- sorption zone (δ), time involved in establishing the primary adsorption zone (t_x), time required by primary adsorption zone to move down its length (t_δ), time of initial formation of primary adsorption zone (t_f), fractional capacity of the prepared column (f), mass rate of flow to the adsorbent (F_m) and percent saturation of column at break point were calculated by using following equations (1-5),

$$t_x = \frac{V_x}{F_m} \tag{1}$$

$$t_\delta = \frac{V_x - V_b}{F_m} \tag{2}$$

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x + t_\delta(f-1)} = \frac{(V_x - V_b)}{V_b + f(V_x - V_b)} \tag{3}$$

$$f = 1 - \frac{t_f}{t_\delta} = \frac{M_s}{(V_x - V_b)C_o} \tag{4}$$

$$\text{Percentage saturation} = \frac{D + \delta(f-1)}{D} \times 100 \tag{5}$$

where, C_o is the concentration of the dye solution percolated into the column, C_b is the concentration of dye at 2% adsorption, C_x is the concentration of dye at 90% adsorption, V_x is the volume of effluent at 90% adsorption, V_b is the volume of effluent at 2% adsorption, M_s is the amount of adsorbate adsorbed in the primary adsorption zone from break point to exhaustion and D the length of column. The break- through curve was used to find out the values of V_b, V_x, C_b *and* C_x, which were then applied to calculate values of t_x, t_f, t_δ, f, δ and percentage saturation at break point.

3. Results and Discussion

3.1. Column Adsorption

Figure 2 shows the break through curve for the system indicating the adsorption process of the adsorbent–adsorbate system in column mode.

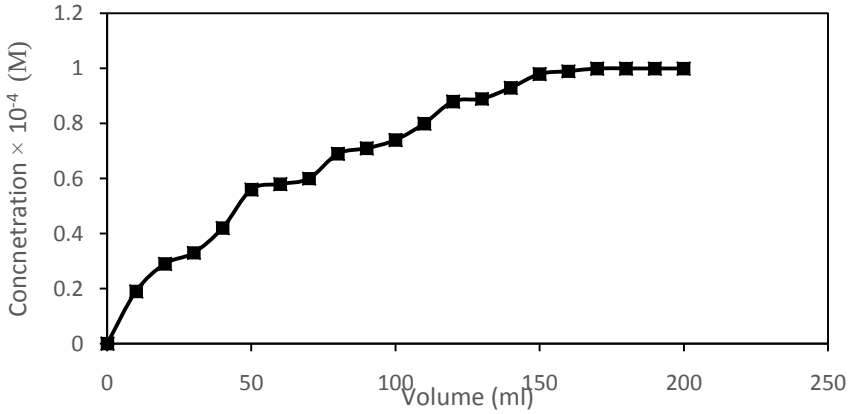


Figure 2. Break through curve obtained during column adsorption for Direct red 81 onto Argemone Mexicana seeds

From the break through curve, it was found that the adsorbent adsorbs 3.66 mg of the dye from 13.51 mg of the dye presented in the solution. F_m was found to be 0.028 mg/cm^2/min for the elected adsorbent (Table 2). Values for t_x, t_δ and t_f was found to be 5281.50, 4929.40 and 30 min respectively as mentioned in table 3 for the adsorbent. It is interesting to note that the percentage saturation of the column was found to be 98.33%.

Table 2. Fix bed adsorber calculations

C_o (M)	C_x (M)	C_b (M)	V_x (ml)	V_b (ml)	F_m (mg/cm^2/min)
10^{-4}	0.98×10^{-4}	0.19×10^{-4}	150	10	0.028

Table 3. Parameters for fixed bed adsorber

t_x (min)	t_δ (min)	t_f (min)	f	δ (cm)
5281.50	4929.40	30.30	0.99	1.87

3.2. Desorption Study

The recovery of Direct red 81 dye and adsorbent was achieved by eluting NaOH through the exhausted fixed bed of the column. It is apparent from Figure 3 the graph that maximum attrition of the column took place with first 10 ml of NaOH and rest of the Direct red 81 was desorbed by eluting ten increments of 10 ml each. Total percentage recovery of the dye was almost 83.03%. Break through capacity of the column was achieved by loading the dye solution of known concentration and desorbing the columns several times.

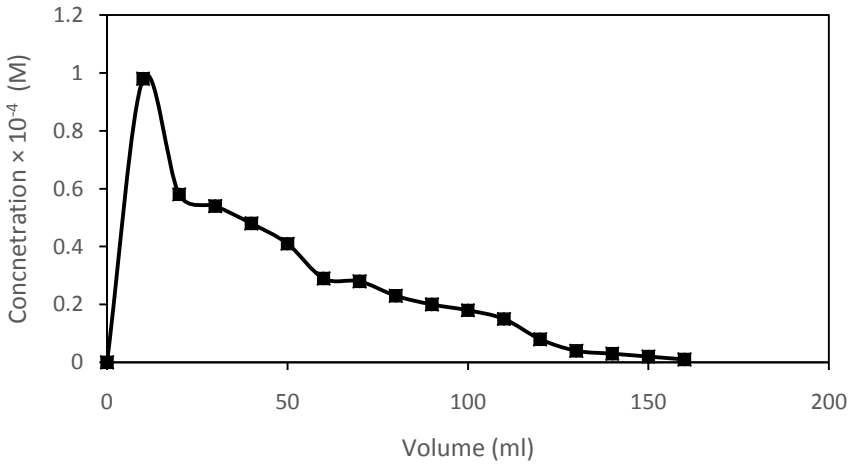


Figure 3. Desorption of Direct red 81 from Argemone Mexicana seeds column

4. Conclusion

Feasibility of adsorption of Direct red 81 onto Argemone Mexicana seeds was evaluated by adopting fixed bed column adsorption method. Results clearly suggested

that the chosen adsorbent can economically and effectively adsorb dye. Bulk removal of dye through column operation recommended that desorption of the dye can be successfully carried out by using NaOH solution with about 83.03% recovery of Direct red 81 from Argemone Mexicana seeds. Thus Argemone Mexicana proved to be an efficient adsorbent for removal of Direct red 81 dye.

5. Acknowledgement

One of the Authors (SK) is thankful to the financial support provided by Symbiosis International University to carry out this research under Junior Research Fellowship programme.

References

1. Mc Mullan, G., Meehan, C., Conneely, A., Kirby, N., Robinson, T., Nigam, P., & Smyth, W. F. (2001). Microbial decolourisation and degradation of textile dyes. *Applied Microbiology and Biotechnology*, *56*(1-2), 81-87.
2. Mittal, A., Kaur, D., Malviya, A., Mittal, J., & Gupta, V. K. (2009). Adsorption studies on the removal of coloring agent phenol red from wastewater using waste materials as adsorbents. *Journal of Colloid and Interface Science*, *337*(2), 345-354.
3. Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, *77*(3), 247-255.
4. Gottlieb, A., Shaw, C., Smith, A., Wheatley, A., & Forsythe, S. (2003). The toxicity of textile reactive azo dyes after hydrolysis and decolourisation. *Journal of Biotechnology*, *101*(1), 49-56.
5. Liu, Q. S., Zheng, T., Wang, P., Jiang, J. P., & Li, N. (2010). Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. *Chemical Engineering Journal*, *157*(2), 348-356.
6. Namasivayam, C., & Kavitha, D. (2002). Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes and Pigments*, *54*(1), 47-58.
7. Ahmad, M. A., Ahmad, N., & Bello, O. S. (2014). Adsorptive Removal of Malachite Green Dye Using Durian Seed-Based Activated Carbon. *Water, Air, & Soil Pollution*, *225*(8), 1-18.
8. Chern, J. M., & Wu, C. Y. (2001). Desorption of dye from activated carbon beds: effects of temperature, pH, and alcohol. *Water Research*, *35*(17), 4159-4165.

9. Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource Technology*, *97*(9), 1061-1085.
10. Khattri, S. D., & Singh, M. K. (2009). Removal of malachite green from dye wastewater using neem sawdust by adsorption. *Journal of Hazardous Materials*, *167*(1), 1089-1094.
11. Pavan, F. A., Mazzocato, A. C., & Gushikem, Y. (2008). Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. *Bioresource Technology*, *99*(8), 3162-3165.
12. Chung, K. T., & Stevens, S. E. (1993). Degradation azo dyes by environmental microorganisms and helminths. *Environmental Toxicology and Chemistry*, *12*(11), 2121-2132.
13. Sivakumar, B., Karthikeyan, S., & Kannan, C. (2010). Film and pore diffusion modeling for the adsorption of Direct red 81 on activated carbon prepared from balsamodendron caudatum wood waste. *Digest Journal of Nanomaterials and Biostructures*, *5*(3), 657-665.
14. Brahmachari, G., Gorai, D., & Roy, R. (2013). Argemone Mexicana: chemical and pharmacological aspects. *Revista Brasileira de Farmacognosia*, *23*(3), 559-567.
15. Das, M., & Khanna, S. K. (1997). Clinicoepidemiological, toxicological, and safety evaluation studies on argemone oil. *CRC Critical Reviews in Toxicology*, *27*(3), 273-297.
16. Shaukat, S. S., Siddiqui, I. A., Khan, G. H., & Zaki, M. J. (2002). Nematicidal and allelopathic potential of Argemone Mexicana, a tropical weed. *Plant and Soil*, *245*(2), 239-247.
17. Mittal, A., Kaur, D., & Mittal, J. (2009). Batch and bulk removal of a triarylmethane dye, Fast Green FCF, from wastewater by adsorption over waste materials. *Journal of Hazardous Materials*, *163*(2), 568-577.
18. Gupta, V. K., Mittal, A., Krishnan, L., & Gajbe, V. (2004). Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Separation and Purification Technology*, *40*(1), 87-96.
19. Adak, A., Bandyopadhyay, M., & Pal, A. (2006). Fixed bed column study for the removal of crystal violet (CI Basic Violet 3) dye from aquatic environment by surfactant-modified alumina. *Dyes and Pigments*, *69*(3), 245-251.

20. Weber, W. J. (1972). *Physicochemical processes for water quality control*. Wiley interscience.