Comparative Sorptive Removal of Direct Red-28 dye from Water Using Acid, Base and 2-Propanol Treated Okra Stem Powder

¹RABIA REHMAN*, ²AADIL ABBAS, ²SHAHZAD MURTAZA, ¹TARIQ MAHMUD

¹Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan. ²Department of Chemistry, University of the Gujrat, Gujrat, Pakistan. grinorganic@yahoo.com*

(Received on 24th April 2012, accepted in revised form 2 July 2012)

Summary: Use of agro-waste material for adsorption is studied now-a-days extensively. But the main problem is their low adsorption capacity as compared to synthetic adsorbents. So, in the following study, adsorption capacity of Okra stem powder had been investigated after chemical modification by acid, base and 2-propanol for adsorption of Direct Red-28 dye from water in batch mode. The results indicated that as compared to untreated biosorbent , acid treated and 2-propanol treated biosorbents had more adsorption capacity, i.e.: 1.86, 2.74 and 6.61 mg.g⁻¹ correspondingly, whereas base treated biosorbent had lower adsorption capacity for this anionic dye, i.e.1.02 mg.g⁻¹.

Keywords: Okra stem, Direct Red-28 dye, adsorption, chemical modification.

Introduction

The rapid industrialization and urbanization resulted in large amounts of waste, which is either directly or indirectly discarded into water streams and adjacent land. Majority of colored effluents of various industries comprised of synthetic organic dyes, which are difficult to biodegrade [1-3]. That's why, various man-made methodologies have been investigated and employed for removal of these dyes from waste-water, so that they could not harm aquatic life especially and ecosystem generally, e.g.: coagulation, biological treatments, micellar enhanced ultrafiltration, oxidation, ozonations, nano-filtration, ultra-filtration and nano-filtration, adsorption onto agricultural solid waste, bentonites, various types of activated carbon or surfactant impregnated montmorillonite [4-7]. Recently, scientists have used highly effective, cheap and locally available adsorbents for the removal of dyes and other contaminants like orange peels, radish peels, banana pith, bamboo dust, pine leaves, rice husk, Jamun seeds, bentonite, neem leaves, peanut husk, perlite, coconut and groundnut shells, duck weed, wheat husk, gram husk, grasses, bagasse, melon rind, mango peels and de-oiled soya [8-11].

There are different varieties of synthetic dyes based on functional groups like; azo, anthraquinone, acidic, basic, disperse and metal complexes which are being used in textile printing and dyeing, paper, rubber, plastics and leather industries [10]. Direct Red-28 dye is chief anionic azo dyes having a benzidine-based structure as shown in Fig.1. It is commonly known as Cong Red. Many Red dyes having better fastness properties, but mostly they are more expensive than Direct Red-28. In spite of this cost effectiveness, it has many detrimental effects because it metabolized and

^{*}To whom all correspondence should be addressed.

converted to benzidine, which is a notorious human carcinogen. Direct exposure to this dye leads to allergic reactions and anaphylaxis [12-18]. So, its removal from waste streams is crucial before discharge into fresh water streams.

We are using Okra (Common name: Lady Finger and Bhindi, and Botanical name: *Abelmoschus esculentus*, family: Malvaceae) stem for the elimination of Direct Red-28 dye after chemical modifications. It is an annual or perennial flowering plant, usually grows to 2 m tall and generally cultivated in warm tropical regions of the world for its fibrous pods. Its stem is hollow, fibrous and mucilaginous, having spiky texture. Because of this, it is not employed in fuel or fodder. Previous studies have been conducted to remove the toxic metal ions using its leaves which showed its ability to use as adsorbent [19-21].



Fig. 1: Chemical structure of Direct Red-28.

Results and Discussion

1. Adsorbent Characterization

Alam and Khan compositional analysis of Okra stem powder revealed that 67.5 % cellulose, 7.1 % lignin, 3.4 % pectic substances, 3.9 % fatty matter and 2.7 % aqueous extractable matter is present in it [20]. Surface characterization of Okra stem powder was carried out by FT-IR spectroscopy and results are presented in Table-1, which is clearly indicating the presence of different functional groups like alkenes, aromatic rings, carbonyl, ester, ketone, alcohol, carboxylic acid. Absorption peaks values varied from already reported values in literature due to differences in regional, climatic and seasonal conditions of growing areas of Okra plant [19, 21].

Table-1: Characteristic vibrational frequencies of Okra stem powder FT-IR spectrum.

Vibrational Assignment	Wave number			
	(cm ⁻¹)			
О-Н	Broad band in			
	3600-3100 range			
C-H stretching	2920, 2852			
C=O stretching	1739			
C=C stretching of aromatic ring	1517			
CH ₂ symmetric bending	1432			
C=O stretching vibration of the acetyl group	1381, 1245			
C-H and C-O of aromatic ring (bending)	1368, 1322			
anti-symmetrical deformation of the C-O-C	1156			
C-O (stretching)	1035			

2. Effect of Particle Size

The influence of biosorbent particle size on its removing efficiency is shown in Fig. 2. Smaller particle size provided more surface area and resulted in higher adsorption capacity [14]. B.T.B removes maximum dye (75.25%) at 80-100 mesh size particles. This is attributed to increase in the accessibility of the Direct Red-28 dye molecules to the pores of the okra stem with the decrease in particle size. A.T.B showed maximum adsorption (92.31%) at 60-80 mesh size particles, whereas U.T.B showed maximum adsorption (90.86%) for 40-60 mesh size particles, P.T.B showed maximum adsorption (92%) for 20-40 mesh size particles and its adsorption rate decreased with enlarging mesh size of okra stem. This is due to the non-availability of further vacant adsorption sites [18].

3. Effect of Biosorbent Dose

The adsorption of Direct Red-28 on acid treated, base treated, untreated and 2-propanol treated Okra stem powder were determined by changing the quantity of biosorbent (0.5-2.5 g) in the dye solution while the starting dye concentration (25 mg.L⁻¹), temperature ($25\pm1^{\circ}$ C) and pH (7.0) were kept constant. As shown in Fig. 3, B.T.B removes maximum dye (76.35%) at 1.0 g biosorbent dose and then removing efficiency decreased rapidly onwards. U.T.B and P.T.B behaved in similar fashion, giving adsorption maxima 87.20% and 85% at 1.0 g dose, while A.T.B removes maximum dye (96.56%) at 1.5 g dose.



Fig. 2: Comparative graph showing effect of particle size on percentage age adsorption of Direct Red-28 using untreated and chemically treated Okra stem powder.

Further increase in biosorbent dose results in agglomeration of biosorbent particle, which reduces the exposure of active binding sites in Okra stem powder. Thus reducing contact between binding sites and Direct Red-28 molecules in aqueous phase led to reduction in adsorption efficiency at higher doses [12, 18].





4. Effect of Contact Interval between Biosorbent and Dye Solution

Its effect on the adsorption process was studied for starting concentration of dye (25 mg.L⁻¹) and biosorbent dose 0.5g and results are shown in Fig. 4. It is observed that B.T.B removes 76.91% dye in 50 minutes but U.T.B showed maximum adsorption of 91.06% at 60 minutes. Whereas A.T.B and P.T.B removed 98 % of Direct Red-28 dye in just 10 and 20 minutes respectively. After maximum removal of dye molecules by adsorption, it becomes almost constant with increasing time. This indicated that, removal of dye by adsorption occurred rapidly

initially on the external surface of the Okra stem powder following slower diffusion into its interior parts [15].



Fig. 4: Comparative graph showing effect of contact time between adsorbent and dye solution on percentage adsorption of Direct Red-28 using untreated and chemically treated Okra stem powder.

5. pH Effect

pH influences the chemistry of dye molecules and adsorption sites in aqueous effectively; So, its optimum conditions were investigated and results are shown in Fig. 5. The pH of a solution affects the degree of ionization and speciation of dye and the overall surface charges of the biosorbent [16].



Fig. 5: Comparative graph showing effect of pH on percentage adsorption of Direct Red-28 using untreated and chemically treated Okra stem powder.

As seen from the Fig. 6, the adsorption of the dye varied in between 90 and 100%. B.T.B showed maximum removal of dye (94.03 %) at pH 4, while U.T.B (96.48 %) at pH 8. Its removal efficiency decreases on either side. A.T.B showed best removal efficiency of 97.76 % at pH 3 and P.T.B at pH 5 removed 95 %. In acidic pH range, the biosorbent surfaces became positively charged attracting

additional anionic dye molecules and enhancing chelating ability of okra stem powder.

6. Effect of Agitation Rate

Its effect on biosorption of Direct Red-28 dye by Okra stem powder was investigated and results are presented graphically in Fig. 6. B.T.B and U.T.B adsorbed maximum 83.58% and 88.43% at 150 rpm. The adsorption results with A.T.B and P.T.B revealed that their adsorption efficiency were nearly in effected by agitation rate with maximum adsorption of Direct Red-28 dye at 150 rpm.



Fig. 6: Comparative graph showing effect of agitation speed on percentage adsorption of Direct Red-28 using untreated and chemically treated Okra stem powder.

It was found that adsorption efficiency improved with decline in agitation speed. By enhancing speed, there was no increase in adsorption. This is due to the fact that all binding sites had been utilized and no further binding sites were available for more adsorption of dye molecules. It also reduces the film boundary layer formation of dye molecules around the biosorbent particles, thus increasing the external film diffusion rate [17].

7. Effect of Dye Solution Temperature

The removing capacity of Okra stem powder for adsorption of Direct Red-28 dye at various temperatures indicated a change in the adsorption efficiency. This effect is shown in Fig. 7. Higher temperature assist the adsorption of Direct Red-28 dye molecules on biosorbent because their mobility enhanced by rising temperature, and it is suggested that the dye molecules interact more effectively with the binding sites on adsorbent. Increasing temperature produces a swelling effect of biosorbent which helps the larger dye molecules to penetrate further into vacant sites. But decrease in the sorption capacity of the Direct Red-28 dye indicated that a high temperature does not favor dye removal. B.T.B and U.T.B showed variation in adsorption capacity with maximum removal of dye at 20 $^{\circ}$ C and 40 $^{\circ}$ C respectively. Whereas P.T.B gave maximum dye removal at 50 $^{\circ}$ C and A.T.B showed decrease in dye adsorption with increase in temperature. It gave maximum dye removal of 97.81 % at 10 $^{\circ}$ C. This unusual parameters in case of A.T.B, may be attributed to the reason that at higher temperatures, movement of the dye molecules decreased, which results in their settlement on adsorption sites [18, 21-24].



Fig. 7: Comparative graph showing effect of temperature on percentage adsorption of Direct Red-28 using untreated and chemically treated Okra stem powder.

8. Isothermal and Thermodynamical Investigations

The adsorption equilibrium data were tested with Langmuir and Freundlich isothermal model for determine mechanism of dye adsorption. Langmuir isotherm equation is given in equation 1:

$$\frac{1}{q} = \frac{1}{bq_m C_o} + \frac{1}{q_m} \quad (\text{Eq. 1})$$

where the term 'q' (mg.g⁻¹) is the amount of dye adsorbed, and ' q_m ' and 'b' are Langmuir constants. Freundlich model is given in equation 2:

J.Chem.Soc.Pak.,Vol. 35, No.1, 2013 92

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (Eq. 2)$$

where ${}^{\prime}K_{\rm F}$ is Freundlich constant and ${}^{\prime}n'$ is the heterogeneity factor. Langmuir Separation factor ${}^{\prime}R_{\rm L}$ was calculated with Eq. 3:

$$R_{L} = \frac{1}{(l_{o} + bC_{o})}$$
 (Eq. 3)

For calculating ' ΔG^{o} ' Eq. 4 was used:

$$\Delta G^{o} = -RT \ln K \qquad (Eq. 4)$$

Here ' ΔG^{o} ' is in KJ.mol⁻¹, '*R*' is gas constant, '*T*' is temperature in Kelvin and '*K*' is the reciprocal of Langmuir constant '*b*' [12, 18].

All these parameters were studied after applying respective optimized operational conditions and resulting data is given in Table-2. Maximum adsorption intensity q_m ' values were in the following order: B.T.B < U.T.B < A.T.B < P.T.B. It revealed that acid and 2-propanol treatment of the biosorbent enhanced its adsorption capacity, whereas base treatment of the adsorbent decreased its efficiency. The resulting values of 'b' revealed that adsorption would not be favored with increasing temperature due to its exothermic nature. Whereas ' K_F ' (the binding constant of adsorption capacity) values indicated that acid and 2-propanol treated biosorbents had more adsorption capacity by physiosorption means. R^2 values of both models are close to unity, which means that both physiosorption and chemisorption phenomenon are involved in dye removal using Okra stem powder. But chemisorption is involved more, because correlation coefficient values of Langmuir model are greater than Freundlich model. The value of n' ranging 1-8 signifies strong physiosorption, which is an important factor after chemical modification, because acid and base treatment hydrolyze lignin and pectic substances found in agro-waste materials, so more surface area become available for sorptive removal of pollutant [10]. Here base treated biosorbent showed poor adsorption of anionic dye, but these types of modifications are beneficial for the removal of cationic dyes [2-6, 18].

Table-2: Isothermal parameters for adsorption of Direct Red-28 dye by untreated, acid treated, base treated and 2-propanol treated Okra stem powder.

Biosorbent	Langmuir Isotherm Parameters				Freundlich Isotherm Parameters					
	Slope	Intercept	\mathbf{R}^2	q _m (mg. g ⁻¹)	b (L. g ⁻¹)	Slope	Intercept	\mathbf{R}^2	K _F	n
U.T.B	3.962	0.538	0.98	1.86	0.136	0.717	-0.915	0.96	0.12	1.394
A.T.B	0.047	0.365	0.98	2.74	7.760	0.251	-0.3	0.92	0.5	3.975
B.T.B	49.716	0.979	0.98	1.02	0.020	8.448	-0.932	0.95	0.12	0.118
P.T.B	0.482	0.151	0.98	6.61	0.314	0.641	0.092	0.97	1.24	1.561

Separation factor values are lower than unity in all cases, i.e. 0.13, 0.003, 0.5, 0.06 U.T.B, A.T.B, B.T.B and P.T.B respectively, showing that adsorption of Direct Red-28 dye was favorable with Okra stem powder. The feasibility of use of Okra stem powder for adsorption is also indicated by ΔG^{o} values, which are -4.94, 5.086, -9.69 and -2.87 KJ.mol⁻¹ for U.T.B, A.T.B, B.T.B and P.T.B correspondingly. These negative values of ΔG^{o} predict the feasibility of use of Okra stem powder use at larger scale is as like as on the batch scale [12, 18].

Experimental

Reagents and Instrumentation Used

Direct Red-28 dye (MW: 696.66 g/mol, λ max: 500 nm), HCl, NaOH, 2-propnol, 1-butanol, formaldehyde, acetone, methanol, ethanol, disodium salt of EDTA, urea, thiourea, antharanilic acid were purchased from Merck and Fluka. UV-Vis Double Beam spectrophotometer (UVD-3500, Labomed) and FT-IR spectrometer (Perkin Elmer, ATR) were used. Okra stems were collected from rural areas of Gujrat (Pakistan). After washing and sun drying for a week, they were crushed into fine powder and preserved in plastic jars [18].

Chemical Treatment of Biosorbent

Generally acid or base treatment is carried out for removal of organic pollutants. Base treatment usually obliterates autolytic enzymes which cause decay of agrowaste material. Whereas acid treatment improves surface area and porosity of biosorbent by producing oxygen surface complexes [22]. Okra stem powder was soaked in 500 mL of 0.01 M HCl and 0.01 M NaOH for 5-6 hours separately and then after filtering and air drying, they were dried in oven at 90 °C for 2-3 hour. They were labeled as A.T.B (acid treated biosorbent) and B.T.B (base treated biosorbent). To find other chemicals suitable for its modification, 5.0 g of Okra stem powder was treated with 50 mL of different locally available water miscible solvents (like: 1-butanol, formaldehyde, acetone, methanol, ethanol) and chelating agents (10 % solution of disodium salt of EDTA, urea, thiourea, antharanilic acid) and employed for adsorption of Direct Red-28 dye. Results given in Fig. 8 indicated that 2-propanol is more effective as compared to other chemicals because it remove lipids and proteins that mask binding sites. It also helps in removing surface impurities and rupturing cell-membrane, which subsequently results in exposure of more binding sites for dye adsorption [22-24]. So for P.T.B (2-propanol treated biosorbent), 50.0 g of Okra stem

powder was soaked in 500 mL of 10% solution 2-propanol for 2 hours, filtered out and then dried as mentioned before at 105 $^{\circ}$ C [18].



Fig. 8: Comparison showing effect of modification of Okra stem powder using different chemicals on percentage adsorption of Direct Red-28.

Adsorption Experiments

All the operational conditions were optimized as described by Rehman *et al.*, [18]. The % age adsorption of dye at any instant of time was calculated using Eq.5:

% age adsorption of dye =
$$\frac{C_{\circ} - C_{\circ}}{C_{\circ}} \times 100$$
 (Eq.5)

Here 'C_o' and 'C_e' are the starting and after experiment concentrations of Direct Red-28 dye in $mg_{.}L^{-1}[18]$.

Conclusion

From this study, it can be safely concluded that Okra stem powder is a very effective biosorbent for removal of anionic dyes from waste water. Its adsorption capacity can be almost doubled by chemical modification with acid and 2-propanol for removing anionic dyes especially. Optimized conditions were as followed: for U.T.B.: 40-60 μ mesh size particles, 1.0 g biosorbent dose, 60 minutes contact time, pH 8, 150 rpm agitation rate and 40 $^{\circ}$ C temperature. For B.T.B.: 80-100 mesh size particles, 1.0 g biosorbent dose, 50 minutes contact time, pH 4, 150 rpm agitation rate and 20 °C temperature. For A.T.B.: 60-80 µ mesh size particles, 1.5 g biosorbent dose, 10 minutes contact time, pH 3, 150 rpm agitation rate and 10 °C temperature. For P.T.B.: 20-40 µ mesh size particles, 1.0 g biosorbent dose, 20 minutes contact time, pH 5, 150 rpm agitation rate and 50 °C temperature. Using these optimized conditions, they can be used for Direct Red-28 dye removal from water on larger scale.

References

- V. Vimonses, S. Lei, B. Jin, C. W. K. Chow and C. Saint, *Applied Clay Science*, 43, 465 (2009).
- A. Mittal, J. Mittal, A. Malviya and V. K. Gupta, Journal of Colloid and Interface Science, 340, 16 (2009).
- 3. G. Crini, *Bioresource Technology*, **97**, 1061 (2006).
- M. C. S. Reddy, L. Sivaramakrishna and A. V. Reddy, *Journal of Hazardous Materials*, 203, 118 (2012).
- R. Rehman, J. Anwar, T. Mahmud, M. Salman and U. Shafique, *Journal of the Chemical Society of Pakistan*, 33, 515 (2011).
- R. Rehman, J. Anwar, T. Mahmud, M. Salman, U. Shafique and W. Zaman, *Journal of the Chemical Society of Pakistan*, 33, 598 (2011).
- B. Acemioglu, Journal of Colloid and Interface Science, 274, 371 (2004).
- L. Lian, L. Guo and C. Guo, Journal of Hazardous Materials, 161, 126 (2009).
- C. Namasivayam and D. J. S. E. Arasi, Chemosphere, 34, 401 (1997).
- K. G. Bhattacharyya and A. Sharma, *Journal of Environmental Management*, 71, 217 (2004).
- 11. C. Namasivayam and D. Kavitha, *Dyes and Pigments*, **54**, 47 (2002).
- Z. Zhang, L. Moghaddam and I. M. O'Hara and W. O. S. Doherty, *Chemical Engineering Journal*, **178**, 122 (2011).

- 13. R. Ahmad and R. Kumar, *Applied Surface Science*, **257**, 1628 (2010).
- I. D. Mall, V. C. Srivastava, N. K. Agarwal and I. M. Mishra, *Chemosphere*, **61**, 492 (2005).
- 15. G. C. Panda, S. K. Das and A. K. Guha, *Journal of Hazardous Materials*, **164**, 374 (2009).
- 16. Z. Hu, H. Chen, F. Ji and S. Yuan, *Journal of Hazardous Materials*, **173**, 292 (2010).
- 17. H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard and J. M. Herrmann, *Applied Catalysis* B: *Environmental*, **39**, 75 (2002).
- R. Rehman, A. Abbas, S. Murtaza, T. Mahmud, W. Zaman, M. Salman and U. Shafique, *Journal* of the Chemical Society of Pakistan, 34, 112 (2012).
- 19. M. Duldulao, H. Watanabe, Y. Kamaya and K. Suzuki, *Wood Industry*, **65**, 256 (2010).
- M. S. Alam and G. M. A. Khan, Journal of Textile and Apparel Technology and Management, 5, 1 (2007).
- I. M. De Rosa, J. M. Kenny, M. Maniruzzaman, M. Moniruzzaman, M. Monti, D. Puglia, C. Santulli and F. Sarasini, *Composites Science and Technology*, **71**, 246 (2011).
- 22. H. N. Bhatti, B. Mumtaz, M. A. Hanif and R. Nadeem, *Process Biochemistry*, **42**, 547 (2007).
- R. Rehman, J. Anwar and T. Mahmud, *Journal* of the Chemical Society of Pakistan, 34, 460 (2012).
- F. Kanwal, R. Rehman, T. Mahmud, J. Anwar and R. Ilyas, *Journal of the Chilean Chemical Society*, 57, 1058 (2012).