Removal of Alizarin Red S (Dye) from Aqueous Media by using Alumina as an Adsorbent

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Summary: Adsorption is potentially an attractive methodology for removing hazardous dyestuff and heavy metals from industrial effluents. In this work the removing efficiency of an industrially important dye Alizarin Red S from aqueous media using alumina as adsorbent has been investigated. Various parameters, which can influence the adsorption like, mesh size of adsorbent, contact time of solution with adsorbent, temperature, pH, adsorbent dose and stirring speed were optimized.

Introduction

Industrial, agricultural and domestic wastes, due to the rapid growth in the technology, are discharged in the several receivers. Mostly, this discharge is channelized to the nearest water sources. Textile dyeing process is a significant source of contamination responsible for the environmental pollution. To meet the demand of textile industry a large variety of dyes are annually produced in tremendous quantities (7 x 10^5 Tones) in the world. The volume of wastewater containing processed textile dyes is on steady increase. As being the derivatives of aromatic compounds, with halo, nitro, and sulpho grouping in their structures most of these are toxic and carcinogenic in nature and pose serious environment threats to human beings as well as aquatic life when present in industrial effluents. Many physical, chemical, and biological methods are employed to eliminate dyes from the wastewater. Physical methods are preferred over chemical and biological methods, because firstly they are simple and inexpensive and secondly do not produce byproducts in water bodies [1-3].

The following study has been conducted to have a great deal with the removal of Alizarin Red S from water. Alizarin red S has been extensively employed since ancient times for dyeing textile material [4].

Alizarin Red S (1,2-dihydroxy-9,10-anthraquinonesulfonic acid sodium salt, ARS, Alias Mordant Red 3, C.I. no. 58005, Fig. 1) is a water-soluble, widely used anthraquinone dye. It is synthesized by sulfonation of alizarin which is a natural dye obtained from madder (*Rubia tinctorum*, *L. Rubiaceae*). In clinical practices, it is also used to stain synovial fluid to assess for basic calcium phosphate crystals. Anthraquinone dyes like ARS are durable pollutants, released especially by textile industries in the aquatic ecosystems. Removal of these from industrial wastewaters is a crucial process, from both economical and environmental points of view [5].

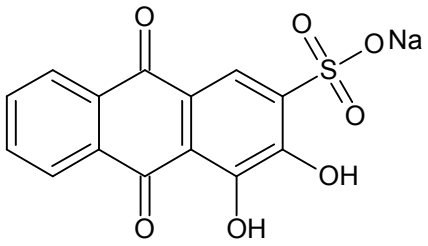

Fig. 1: Alizarin Red S.

In this study Alumina is used as an adsorbent. Chemically this is Al_2O_3. It is extensively used as an adsorbing material for metal ions like; chromium [6], cadmium, lead [7], calcium, strontium, thallium [8], thorium [9], arsenic, selenium and vanadium [10], anions like; fluoride [11], non metals; like boron [12] and phosphorus [13], organic compounds; like alcohols, phenols [14], carboxymethyl starch [15], sodium alkylbenzene sulfonates [16] and various volatile organic compounds [17], gases; like carbon dioxide [18], sulphur oxides [19], hydrogen peroxide [20] and nitrogen [21]. It can be effectively used for the removal of dyes from wastewater, which is the scope of our present study.

Mostly nanofiltration and anion exchange methodologies are used to remove anionic dyes from water which are expensive to employ on larger scale [22-24].

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Results and Discussion

In order to find the appropriate conditions of particle size of the adsorbent, adsorbent dose, concentration of dye, contact time, pH, stirring speed, and temperature for the adsorption of Alizarin Red S on Alumina, various experiments were conducted. The results of these experiments were as followed.

Effect of Mesh Size

The effect of adsorbent's mesh size was studied in the range of 10-80 microns mesh size (10-30, 30-50, 50-80) for checking the maximum adsorption of Alizarin Red S, and the smallest mesh size (50-80) was shown to be best for adsorption, as particles with smallest size presents a larger surface area and the results are shown in Fig. 2. Mesh size is inversely related with particle size. As the mesh size is larger, the size of particle is accordingly decreased which results in more surface area available for adsorption.

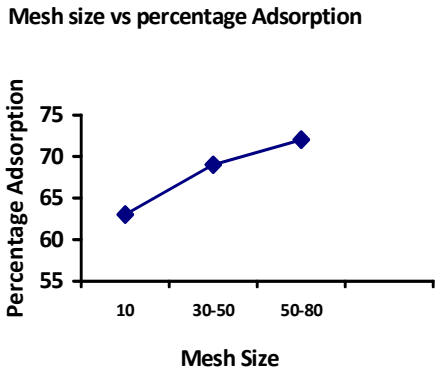

Fig. 2: Effect of mesh size of Alumina on percentage adsorption of Alizarin Red S.
Experimental parameters: Contact time, t (15 min.), initial concentration of dye C_o (25 ppm), adsorbent amount (0.6 g), agitation speed (200 rpm), temperature (30 °C) and solution volume (V) 25 mL).

Effect of Adsorbent Dose

The effect of variation in the adsorbent amount on the process adsorption of Alizarin Red S was studied, with different adsorbent amount in the range of 0.1-1.0 g. The results obtained are shown in Fig. 3. From Fig. 3, it is observed that adsorption increases with increasing amount of Alumina dose. Maximum removal was 71% for dye dose of 25 ppm. The increase in adsorption with increase in amount of Alumina dose is due to the fact that more surface area is available for adsorption or in other words more active sites are available.

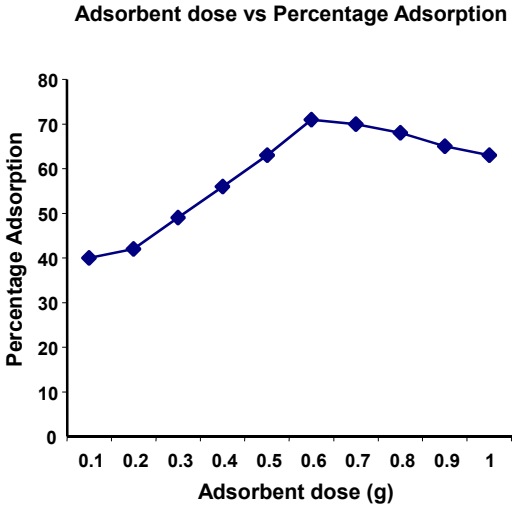

Fig. 3: Effect of adsorbent dose on percentage adsorption of Alizarin Red S.
Experimental parameters: Contact time, t (15 min), initial concentration of dye C_o (25 ppm), agitation speed (200 rpm), temperature (30 °C) and solution volume (V) 25 mL).

Effect of Initial Dye Concentration

Initial dye concentration was one of the effective factors on adsorption efficiency. The percentage of Alizarin Red S adsorption was studied as a function initial dye concentration of in the range of 5-25 ppm. The results obtained are present in Fig. 4. The percentage adsorption increases with increase in initial concentration of the dye for Alumina. It was observed that adsorption yield increased with increase in initial concentration of the dye. Minimum adsorption was 50% for 5ppm concentration to maximum adsorption value 71% for 25 ppm concentration of dye solution. This may be due to available active sites and increase in the driving force of the concentration gradient, as an increase in the high initial concentration of the dye.

Effect of Contact Time

Contact time was one of the effective factors in adsorption process. The percentage of Alizarin red

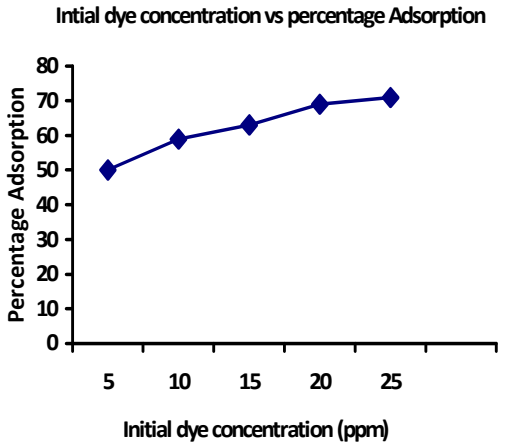

Fig. 4: Effect of initial concentration of dye on percentage adsorption.
Experimental parameters: Contact time, t (15 min), agitation speed (200 rpm), temperature (30 °C) and solution volume (V) 25 mL).

S adsorption was studied as a function of contact time in the range of 15-150 minutes. The results obtained were presented in Fig. 5. It was observed that with the increase of contact time, the percentage adsorptions also increased. Minimum adsorption was 40 % for time 5 minutes to maximum adsorption value 72 % for the time 35 minutes for 25 ppm initial concentration of dye solution. The adsorption characteristic indicated a rapid uptake of the dye. The adsorption rate however decreased to a constant value with increase in contact time because of all available sites was covered and no active site available for binding.

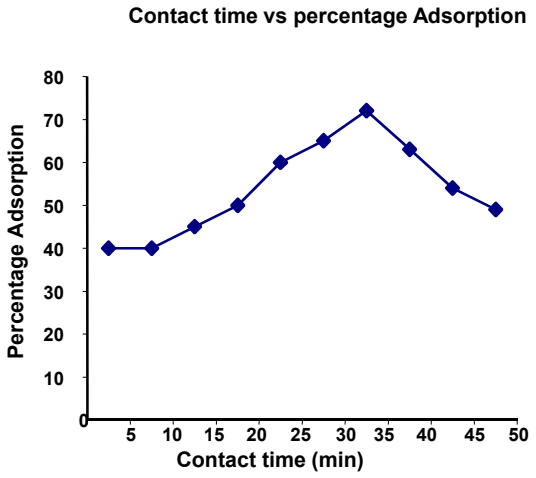

Fig. 5: Effect of contact time of Alumina with Alizarin Red S solution on percentage adsorption.

Experimental parameters: Initial concentration of dye C_o (25 ppm), adsorbent amount (0.6 g), agitation speed (200 rpm), temperature (30 °C) and solution volume (V) 25 mL).

Effect of pH

The pH of the aqueous solution was clearly an important parameter that controls the adsorption process. The percentage of Alizarin Red S adsorption was studied as a function of pH in the range of 1-5. The results obtained were shown in Fig. 6. The minimum adsorption was 41% at pH 5.0 and maximum adsorption was 75% at pH 1.0 for 25 ppm initial concentration of dye solution. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate (Alizarin Red S) and adsorbent (Alumina) that ultimately resulted in the reduced % age adsorption.

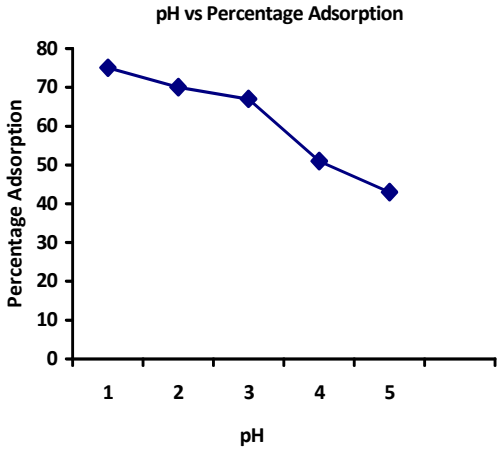

Fig. 6: Effect of pH on percentage adsorption of Alizarin Red S.
Experimental parameters: Contact time, t (15 min), initial concentration of dye C_o (25 ppm), agitation speed (200 rpm), temperature (30 °C) and solution volume (V) 25 mL).

Effect of Stirring Speed

The effect of variation in the stirring speed on the process adsorption of Alizarin Red S was studied. Four different stirring speeds were used in the range of 100-500 rpm. The results obtained were shown in Fig. 7. It was observed that adsorption yield increased with moderate stirring speed. The minimum adsorption was 49 % for speed 500 rpm and maximum adsorption was 73 % for speed 300 rpm for 25 ppm initial concentration of dye solution,

after that, it decreased and there was no further increase in adsorption as all binding sites had been used and no binding sites were left behind.

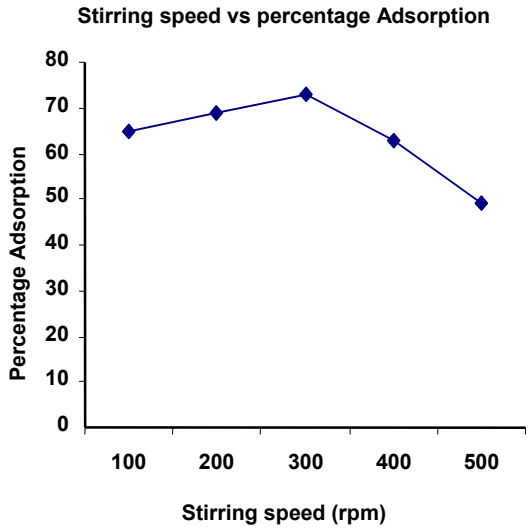

Fig. 7: Effect of stirring speed on percentage adsorption of Alizarin Red S.
Experimental parameters: Contact time, t (15 min), initial concentration of dye C_o (25 ppm), temperature (30 °C) and solution volume (V) 25 mL).

Effect of Temperature

Temperature has an important effect on the rate of adsorption. The percentage of Alizarin Red S adsorption was studied as a function of temperature in the range of 20-50 °C. The results obtained were present in Fig. 8. It was observed that adsorption yield decrease with increase in temperature. The minimum adsorption was 52 % at 50 °C and maximum adsorption was 74 % at 30 °C for 25 ppm initial concentration of dye solution. The decrease in adsorption at high temperature because molecules move with great speed and less time of interaction was available for dye anions with adsorbent material.

Experimental

The adsorption phenomenon of Alizarin Red S was examined as followed.

Chemicals

All chemicals used during experimental work were of analytical grade and were used as such without purification. Alizarin red S (Fluka), HCl (E. Merck 11.6 M). Double distilled water was used for the preparation of all types of solution and dilution when required.

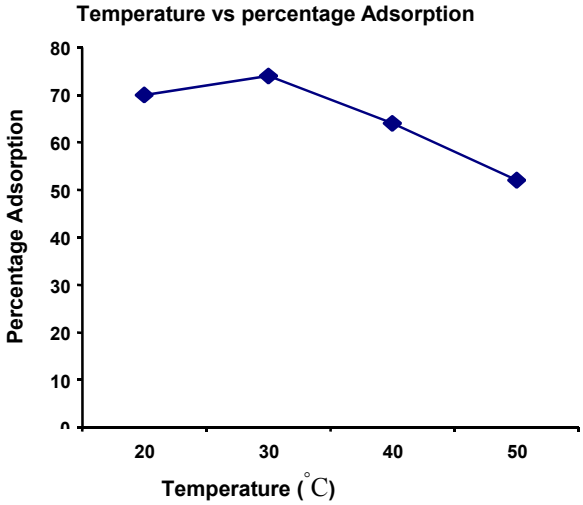

Fig. 8: Effect of temperature on percentage adsorption of Alizarin Red S.
Experimental parameters: Contact time, t (15 min), initial concentration of dye C_o (25 ppm), agitation speed (200 rpm) and solution volume (V) 25 mL).

Instrumentation

Balance ER-120A (AND), Electric grinder (Kenwood), pH meter HANNA pH 211 (with glass electrode), UV/VIS spectrophotometer (Labomed, Inc. Spectro UV-Vis double beam UVD = 3500).

Standard Solutions

1.0 g of Alizarin Red S was taken in 1000 mL measuring flask and dissolved in double distilled water, making volume up to the mark. This was 1000 ppm stock solution of dye. Standard solutions of dye were prepared by successive dilution of stock solution.

Adsorption Experiments

The adsorption studies were carried out at 25 ± 1 °C. pH of the solution was adjusted with 0.1 N HCl. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture were filtered and the remaining dye concentration were determined in the filtrate using (Spectro UV-Vis Double Beam UVD-3500, Labomed.Inco) at λ_{max} = 423 nm.

The effect of various parameters on the rate of adsorption process were observed by varying mesh size of adsorbent (10-80 microns), contact time, t (15-150 min.), initial concentration of dye C_o (5-25 ppm), adsorbent amount (0.1-1.0 g), initial pH of solution (1-5), agitation speed (100-500 rpm) and temperature (20-50 °C). The solution volume (V) was kept constant 25 mL).

The dye adsorption (% age) at any instant of time was determined by the following equation:

$$\text{Dye adsorption (\%)} = \frac{C_o - C_e}{C_o} \times 100$$

where C_o is the initial concentration and C_e is the concentration of the dye at equilibrium.

To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

Conclusion

From the present study, it is concluded that Alumina is a good adsorbent for the removal of the dyes from aqueous media. Optimum conditions for the removal of Alizarin Red S with Alumina are: 0.65 g of adsorbent, dye concentration 25 ppm, at 30 °C, with 35 minutes contact time, 300 rpm agitation speed and at pH 1.0.

References

1. M. J. Iqbal, and M. N. Ashiq, *Journal of Hazardous Materials*, **139** (1), 57 (2007).
2. T. M. Elmorsi, Y. M. Riyad Zeinhom, H. Mohamed, and Hassan M. H. A. El-Bary, *Journal of Hazardous Materials*, **174 (**1-3), 352 (2010).
3. S. Yahya. Al-Degs, I. Musa. El-Barghouthi, H. Amjad, El-Sheikh, and M. Gavin Walker, *Dyes, and Pigments*, **77**, 16 (2008).
4. S. Pirillo, M. L. Ferreira, and E. H. Rueda, *Journal of Hazardous Materials*, **168**, 168 (2009).
5. P. Zucca, C. Vinci, F. Sollai, A. Rescigno, and E. Sanjust, *Journal of Molecular Catalysis A: Chemical*, **288**, 97 (2008).
6. S. Mor, K. Ravindra, and N. R. Bishnoi, *Bioresource Technology*, **98**, 954 (2007).
7. T. K. Naiya, A. K. Bhattacharya, and S. K. Das, *Journal of Colloid and Interface Science*, **333**, 14 (2009).
8. T. L. Roach, and D. M. Himmelblau, *Journal of Inorganic and Nuclear Chemistry*, **17**, 373 (1961).
9. Zhi-Jun Guo, Xing-Min Yu, Fei-Hu Guo, and Zu-Yi Tao, *Journal of Colloid and Interface Science*, **288**, 14 (2005).
10. T. Su, X. Guan, G. Gu, and J. Wang, *Journal of Colloid and Interface Science*, **326**, 347 (2008).
11. S. Ghorai, and K. K. Pant, *Separation and Purification Technology*, **42**, 265 (2005).
12. W. Bouguerra, A. Mnif, B. Hamrouni, and M. Dhahbi, *Desalination*, **223**, 31 (2008).
13. A. Morales, M. M. Ramírez de Agudelo, and F. Hernandez, *Applied Catalysis*, **41**, 261 (1988).
14. D. J. Crisp, *Journal of Colloid Science*, **11**, 356 (1956).
15. Y. Chen, S. Liu, and G. Wang, *Journal of Colloid and Interface Science*, **303**, 380 (2006).
16. K. Nagashima, and F. D. Blum, *Physicochemical and Engineering Aspects*, **176**, 17 (2001).
17. E. Díaz, S. Ordonez, A. Vega, and J. Coca, *Journal of Chromatography A*, **1049**, 139 (2004).
18. E. Baumgarten, and A. Zachos, *Spectrochimica Acta Part A: Molecular Spectroscopy*, **37**, 93 (1981).
19. S. Andersson, R. Pompe, and N. Vannerberg, *Applied Catalysis*, **16**, 49 (1985).
20. A. J. deRosset, C. G. Finstrom, and C. J. Adams, *Journal of Catalysis*, **1**, 235 (1962).
21. D. Dollimore, and J. Pearce, *Powder Technology*, **25**, 71 (1980).
22. H. C. Chiu, C. H. Liu, S. C. Chen, and S. Yi Suen, *Journal of Membrane Science*, **337**(1-2), 282 (2009).
23. R. Jiraratananon, A. Sungpet, and P. Luangsowan, *Desalination*, **130**, 177 (2000).
24. S. Karcher, A. Kornmuller, and M. Jekel, *Water Research*, **36**, 4717 (2002).