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Summary: The adsorption of Murexide from aqueous solution onto the Pomegranate bark was investigated at room temperature. The morphological study presented that the HNO₃ treatment increased the surface roughness of the adsorbent. EDX studies show that the untreated Pomegranate bark had carbon content (52 wt %) and oxygen content (44 wt %) while in the case of HNO₃ treated pomegranate bark, the carbon quantity decreased (42 wt %) and oxygen quantity (52 wt %) increased. The results showed that the adsorption of Murexide dye from aqueous solution was increased as increased the adsorption time and then equilibrium was reached after 30 min of adsorption time. The HNO₃ treated Pomegranate bark (0.73 mg/g), which might be due to increased surface roughness. The adsorption of Murexide was also studied at different pH, which presented that low pH was favorable for the removal of color material from aqueous solution.

Key words: Murexide, Adsorption, EDX, SEM.

Introduction

Dyes and pigments are extensively used in various fields but their discharge into the water reservoirs causes serious environmental pollution. The dyes effluents, which discharged from various industries such as textile, leather, carpeting manufacturing, food processing, pulps and paper and dye manufacturing, are easily detectible. The world wide manufacturers produce more than 7×10^5 tones of different dyes and pigments annually. It was reported that during the dyeing process about 10-15 % of the synthetic dyes are discharge into the environment as waste materials [1]. The removal/adsorption of coloring materials from the effluents is essential in term of environmental point of view because dyes and pigments have large size and complex molecular structures. It also shows stability towards heat and light, non-oxidizable by conventional physical techniques and also resist to biodegradation which disturb the aquatic life [2,3]. To overcome this important environmental issue, adsorption is one of the most effective and economical method as compared to other techniques such as coagulation, membrane technology, and biological treatments. Because it reduce/remove both organic and inorganic waste materials, which left in effluents after the conventional treatment. The relative advantages of adsorption technique include, the easy and safe to operation, no sludge formation, the availability of abundant low-cost materials/adsorbents, and also the adsorbent regeneration is possible [4,5]. Various types of

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adsorbent used for the removal of different types of dyes from waste water. For example, Santhy and Selvapathy used coir pith activated carbon as an adsorbent for the removal of procion reactive orange 12, reactive red 2, and reactive blue 4 [6]. Uzun and Guzel used chitosan and monocarboxy methylated (mcm)-chitosan for the adsorption of dye stuff [orange II, crystalviolet and reactive blue 5] and pnitrophenol from aqueous solution [7]. Zhang et. al., [8] studied the adsorption of dyes such as methylene blue and reactive orange X-GN and phenol from aqueous medium via resin adsorbents (Amberlite XAD-4, amacroreticular adsorbent and ZCH-101). Ishaq et. al. used coal ash as an adsorbent for the removal of tartrazine from aqueous solution [9]. Dogan et. al., [10] adsorbed cationic methyl violet and methylene blue dyes from waste water by sepiolite adsorbent. Alam et. al, [11] removed Triphenylmethane Dye from Aqueous Solution by Carbonaceous Adsorbent.



Fig. 1: Chemical structure of Murexide.

The main objective of our present study is to use Pomegranate bark (low cost adosbent) for the removal of murexide dye from aqueous solution. The murexide was selected because of its irritating effect while Pomegranate bark is a waste material, which was used as an adsorbent for removal of murexide. The murexide was first reported in 18th century, it can be successive treatment of uric acid with nitric acid and then ammonia. Its appearance is reddish purple powder in dry state and slightly soluble in water. Its color is yellow in strong acidic solution, reddishpurple in weakly acidic solutions and blue-purple in alkaline solutions [12]. The murexide may cause eye and skin irritation and when inhaled it may cause respiratory tract irritation to mucous membranes and upper respiratory tract [13]. Some research work is reported on the adsorption of murexide from aqueous solution. For example, Shokrollahi et al., [14] used activated carbon for the the removal of murexide from aqueous solutions and performed the adsorption kinetic and thermodynamic studies. Rehman et al., used rice husk as adsorbent for the removal of murexide dye from aqueous medium. [15]. In our present work, the Pomegranate bark was also treated with HNO₃ in order to study the effect of surface morphology on the murexide adsorption. The adsorption of murexide was also performed at different pH in order to investigate best pH for the maximum adsorption of dye from aqueous medium.

Results and Discussion

Morphological Study of Pomegranate Bark

The morphological study of the Pomegranate bark was carried out with scanning electron microscope (SEM) in order to observe surface roughness/pores within the surface of the adsorbent. Fig. 2a presents the SEM microgram of the untreated Pomegranate bark, which shows that the surface is rough and also small size pores are present on the adsorbent surface. The SEM image (Fig. 2b) of acid treated Pomegranate bark show that the surface roughness of the adsorbent was highly increased after the treatment with HNO₃. It was reported [16] that the surface roughness/pores within the adsorbents play an important role during the adsorption process. They presented that greater the number of pores in the adsorbent greater will be its ability to remove toxic materials from aqueous medium.

EDX Study of Untreated and HNO₃ Treated Pomegranate Bark

EDX is one of the most important instrumental techniques used for the determination of

different elements (percentage) in an adsorbent/any type of materials. Fig. 3 shows the EDX analyses of untreated and HNO₃ treated Pomegranate bark sample, which presented wt % of different elements in adsorbents. The untreated Pomegranate bark (Fig. 3a) showed highest wt % of carbon (52 wt %), oxygen (44 wt %), and potassium (1.1 wt %) while the other elements such as zinc, calcium, chlorine and copper are present in minute quantities. The HNO₃ treated pomegranate bark sample (Fig. 3b) show carbon (42 wt %), oxygen (52 wt %) and nitrogen (3 wt %) while other elements such as magnesium, silicon, aluminum are present in minute quantities. The increase in the wt % of oxygen indicated that HNO₃ treatment might have created different functional groups such as carboxylic, hydroxyl etc., on the surface of Pomegranate bark.



Fig. 2: SEM images of (a) untreated HNO₃ Pomegranate bark samples (b) treated HNO₃ Pomegranate bark samples.

Adsorption Kinetic of Murexide

For the sufficient removal/recovery of the dyes from different sources, the adsorption time should be short enough for the time consuming in experiments in the laboratories as well as for the industrial applications. In this study, the Pomegranate bark was used as an adsorbent for the removal/adsorption of Murexide from aqueous solution. The adsorption of Murexide onto untreated Pomegranate bark and HNO₃ treated Pomegranate bark, as function of time is shown in fig. 4. The adsorption study of Murexide dye onto Pomegranate bark was carried out at room temperature. The result showed that the adsorption of dye is increased as increased the adsorption time. Fig. 4 shows the adsorption of the adsorbate molecules onto untreated Pomegranate bark and HNO₃ Pomegranate bark increased gradually and then level off after 30 min (0.73 and 1.7 mg/g, respectively). The result in fig. 4 also indicated that the HNO3 treated Pomegranate bark adsorbed high quantity of Murexide dye as compared to untreated Pomegranate bark. It might be due to the high surface roughness of HNO₃ treated Pomegranate bark than untreated adsorbent.



Fig. 3: EDX study of (a) untreated HNO₃ Pomegranate bark samples (b) treated HNO₃ Pomegranate bark samples.



Fig. 4: Adsorption of Murexide from aqueous solution on, as a function of time.

Adsorption of Murexide onto Pomegranate Bark at different pH

The adsorption of Murexide dye was also carried out at different pH (2, 4, 7 and 8) at room temperature. Table-1 shows the effect of pH on the removal of Murexide dye by untreated Pomegranate bark and HNO₃ treated Pomegranate bark. Both types of adsorbents adsorbed high quantity of Murexide at low (acidic) pH 2, and its adsorption was decreased gradually as further increase in pH. It was reported [17] that the acid dye is first dissolve in aqueous solution, which is dissociate and convert into anionic dye ions.

 $MXONH_4 \xrightarrow{H_2O} MXO^- + NH_4^+$

Table-1: Adsorption of Murexide onto Pomegranate bark at different pH.

рН	Untreated pomegranate bark (mg/g)	HNO3 treated pomegranate bark (mg/g)
2	1.8	1.88
4	1.05	1.14
7	0.69	0.91
8	0.62	0.81

It was also reported by Mall et al [18] that below pH 7, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. As the pH of the system is increased, the number of negatively charged sites increased and the number of positively charged sites decreased. A negatively charged surface site on the adsorbent did not favour the adsorption of dye anions due to electrostatic repulsion.

Experimental

Materials

Murexide was purchased from Merck chemical company. The Pomegranate bark was dried at room temperature, then crushed and ground into fine powder using grinder. The sample was then screened through a screener ($60 \mu m$ mesh size) and stored for further use.

HNO₃ Treatment of Pomegranate Bark

The Pomegranate bark was treated with 1 M HNO₃ and stirred for 1 h at room temperature. The treated Pomegranate bark powder was then filtered and washed several time with distilled water until free from acid.

Adsorption of Murexide onto Pomegranate Bark

One gram adsorbent and 30 ppm murexide solution (50 mL) was stirred at room temperature for

different time duration separately, and determined the equilibrium time using spectrophotometer-20. The adsorption of murexide solution was also determined at different pH (2, 4 and 8) at room temperature.

Conclusion

The Pomegranate bark was used as an adsorbent for the removal of Murexide from aqueous solution. The high quantity of Murexide was removed by HNO_3 treated Pomegranate bark (1.7 mg/g) than untreated Pomegranate bark (0.73 mg/g). The removal of Murexide from aqueous solution was also studied at different pH, which presented that low pH was favorable for the removal of color material from aqueous solution.

Reference

- 1. M. J. Iqbal and M. N. Ashiq, *Journal of Hazardous Materials*, **139**, 57 (2007).
- M. Ishaq, K. Saeed, I. Ahmad, M. Shakirullah and S. Nadeem, *Tenside Surfactants Detergents*, 1, 7 (2010).
- 3. A. Mittal, L. Kurup and J. Mittal, *Journal of Hazardous Materials*, **146**, 243 (2007).
- 4. K. Mohanty, D. Das and M. N. Biswas, *Chemical Engineering Journal*, **115**, 121 (2005).
- 5. K. A. Halouli and N. M. Drawish, *Separation Science and Technology*, **30**, 3313 (1995).
- 6. K. Santhy and P. Selvapathy, *Bioresource Technology*, 97, 1329 (2006).

- 7. I. Uzun and F. Guzel, *Journal of Hazardous Materials*, **118**, 141 (2005).
- 8. X. Zhang, A. Li, Z. Jiang and Q. Zhang, *Journal of Hazardous Materials*, **137**, 1115 (2006).
- 9. M. Ishaq, K. Saeed and S. Nadeem, *Tenside Surfactants Detergents*, **2**, 130 (2011).
- 10. M. Dogan, Y. Ozdemir and M. Alkan, *Dyes and Pigments*, **75**, 701 (2007).
- S. Alam, F. Mabood, M. Sadiq, Noor-ul-Amin and F. K. Bangash, *Tenside Surfactants Detergents*, 2, 134 (2011).
- 12. http://en.wikipedia.org/wiki/Murexide (2012).
- 13. http://chemicalland21.com/specialtychem/nd/M UREXIDE.htm (2012).
- A. Shokrollahi, M. Ghaedi, M. Ranjbar and A. Alizadeh, *Journal of the Iranian Chemical Society*. 3, 219 (2010).
- R. Rehman, J. Anwar, T. Mahmud, M. Salman, U. Shafique and Waheed-Uz-Zaman, *Journal of* the Chemical Society of Pakistan, 33, 598 (2011).
- M. Ishaq, I. Ahmad, M. Shakirullah, Habib-Ur-Rehman, M. Arsala Khan, I. Ahmad and I. Rehman, *Toxicological and Environmental Chemistry*, 89, 1 (2007).
- 17. I. D. Mall, V. C. Srivastava and N. K. Agarwal, *Dyes and Pigments*, **69**, 210 (2006).
- I. D. Mall, V. C. Srivastava, G. V. A. Kumar and I. M. Mishra, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 278, 175 (2006).