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RICE HUSK AS DYES REMOVAL FROM IMPREGNATED COTTON WASTES GENERATED IN SPORTS INDUSTRIES OF SIALKOT, PAKISTAN

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Abstract

The current study was designed to the potential dyes removal present in solid wastes of cotton (Generated from sports industries). Sport products were colored with different shaded dyes with the help of cotton that are disposed to the different environmental compartment. Cost effective and eco-friendly adsorbents (rice husk) has been collected and used as an ideal alternative to the conventional method of dyes removal for disposed cotton wastes. The effect of pH, contact time, adsorbent dose, shaking speed and amount of dyes solution of rice husks on dyes removal have been evaluated and optimized. Maximum and efficient dyes removal was observed at pH (3.0), contact time (240 min), adsorbent dose (8.0 g), shaking speed (300 rpm) and amount of dyes solution (200 ml). All these conditions have ensured dyes removal up to 91, 93, 92, 90 and 93% respectively. This process highlighted the advantage of recovery of methyl ethyl ketone (MEK) and dyes which may be used again after modification. Furthermore the present study encourages that the rice husks generated as biological waste can be used as promising tool for dyes removal.

Introduction

Sport industries of Sialkot are one of the important export industries of Pakistan, where different dyes are used as coloring agent to the products. Sialkot consist of total 3229 functional industrial units with 900 sport product units and 57 rice husking mills (Qadir *et al*., 2008). A total of 70 factories in Sialkot dealing with dyes and pigment with their 150-300 kg/day production. Dyes are used in football (50-60%), Gloves (20-30%) and others (10%). The total amount of screen printing ink (4000-5000 kg/month) is used in the sports industries. These inks are composed of 60% resins (polyvinyl chloride and poly urethane etc), Dyes 30-35% (cadmium yellow, cobalt violet, cobalt blue, chromium oxide green and Phthalocyanine etc), additives and solvents (methyl ethyl ketone and toluene i.e., carcinogenic). The minimum cotton wastes produced are 5-7 kg/day/factory. The annual demand of pigments and dyes stuff in Sialkot is about 2000 kg. Sports industries and dye/pigment suppliers, first prepared different shades of dyes before applying them onto different sports goods. These dyes shading process and their application produce considerable amount of cotton wastes. Dyes were cleaned up from screens, football pieces and hockey stickers with the help of cotton. The disposed cotton wastes are openly dumped in residential areas or left incinerated at outskirts of the city. These untreated wastes of cotton contain harmful dyes and pigments that become the source of water, soil and air pollution. Heavy metals in the aforementioned wastes also effect the growth of various plant species (Ahmad *et al*., 2012; Khan *et al*., 2013). Dyes in the water bodies emanated from impregnated cotton wastes are of priority concern due to their hazardous effects posing to different life forms. Besides Sports industries, textiles, papers, cosmetics, food, plastic industries also use dyes as a color and enormous volume of water used in this process (Safa & Bhatti, 2011). Such kinds of contaminants make water unfit for the domestic use and for human consumption (Crini, 2006). Therefore there is a dire need of dyes removal prior their discharge to water channel or to the ecosystem from various cotton wastes. Water containing dyes are cleaned prior to their discharge into the ecosystem by various methods like irradiation, ozonation, coagulation, oxidation, precipitation, activated carbon, filtration and adsorption (Gong *et al*., 2005). All these methods are costly, not more effective and efficient but in spite of that dyes removal from industrial waste by Rice husks are preferred as more economical and efficient method. Pakistan is considered to be the fourth world largest rice producing country in the world. Therefore the waste materials produced as rice husks are enormous. This waste produced can be used as most important adsorbent for dyes removal emanating from various industrial wastes.

The current study was aimed in the efficient removal of synthetic dyes from cotton wastes of sports industries by using Methyl Ethyl Ketone (MEK) and to evaluate potential low cost rice husk as adsorbent for dyes removal from dye contaminated water. This study further evaluate and optimize the effect of adsorbent dose, amount of dyes concentration, shaking speed, pH and contact time of rice husk on dyes removal.

Materials and Methods

Sample collection and preparation of adsorbent: Sample of solid wastes (cotton) containing dyes used for coloring to the sport products were collected from different sport industries of Sialkot, Pakistan. Rice husks used for the adsorption of dyes removal were obtained from local mills of Sialkot. The fresh biomass of rice husk was rinsed several times with distilled water in order to eliminate dust and other adhering particles. The rinsed biomass was initially sun dried followed by oven drying at 60^oC for 24 hours. It was weighed after dryingness. Furthermore it was grinded to the desired 1-2 mm mesh size.

Separation of dyes from cotton: Dyes were adsorbed on the surface of cotton (solid wastes); therefore its separation was necessary for its recovery or further treatment. Methyl Ethyl ketone (MEK) was used for the separation of dyes from cotton due to inexpensive and additional benefits of being its low solubility than water (boiling point 89^{o}C). MEK of 700 ml was added to 50 g of waste cotton (containing dyes) along with 300 ml water in 1000 ml beaker. All the solution was prepared in triplicates and overnight stayed to assure maximum dyes removal.

Removal of cotton from solution: After overnight stay of waste cotton most of the dyes detach from the cotton due to presence of MEK. However cotton with traces of dyes was removed from solution. Removed cotton still left with color. Complete decolorization of cotton was not possible due to the absorption of traces of dye color in the threads of cotton.

Recovery of MEK: For the purpose of MEK recovery a conical flask of 500 ml was attached to both ends of condenser. Flask and condenser was fitted with rubbers corks. The solution in the flask was heated up to 100^{o}C. As the temperature reached up to 89^{o}C MEK was recovered completely drop wise and reused for sample preparation next time.

Recovery of dyes from solution: After condensation process of MEK the solution contains dyes and water. The solution was stayed for a while in separating funnel. After 20 minutes a Bi layer of dyes and water was formed. Dyes were separated by separating funnel from the rest of solution and placed in sunlight for drying or used as such for other process.

Adsorption studies: Treatment of water containing dyes was done using rice husk as adsorbent. The effects of various factors on the rate of adsorption process was observed by their Adsorption dose, retention time, dyes concentration, pH and shaking speed.

Effect of adsorption dose: Different quantities of rice husk (2, 4, 6, 8 and 10 g) were weighed and add 100 ml of water to each of the five 250 ml conical flask containing dyes. All the flasks were labeled and covered with aluminum foil to avoid splashing of water during shaking. All the flasks were placed in a wired shaker and shake them for 4 hours to assure adsorption of dye on rice husk. After 4 hours of shaking all the samples were filtered and their absorbance was measured at λ 560 nm by using spectrophotometer.

Effect of contact time: The rice husk of about 8 g and sample of 100 ml were taken in five different flasks at different retention time of 1, 2, 3, 4 and 5 hrs. All the samples were further subjected to shaking and observed the filtrates absorbance.

Effect of shaking speed: To verify the effects of shaking speed on dyes removal five flasks in which 100 ml sample and rice husk of about 8 g were subjected to 100, 200, 300, 400 and 500 rpms. All the samples were shaken for considerable time of 4 hours. The rice husk was removed and check for the absorbance of filtrate.

Effect of pH: The samples containing dyes of 100 ml in five each conical flask (250 ml) was taken and the pH as 3, 5, 7, 9 and 11 was stabilized. A rice husk of 8 g was added to all the samples and shaken at 300 rpms for about 4 hrs followed by the process of filtration. After separation of rice husk, the filtrate was subjected to measurement of absorbance and percentage dyes removal was calculated.

Effect of dyes concentration: The dyes concentration of 100, 200, 300, 400 and 500 ml in five different flasks were taken with 8 g of rice husk and their pH at 3 was adjusted with 0.1 N solutions of HCl and NaOH. After shaking at 300 rpm for about 4 hrs, all the samples filtrate were checked against their absorbance.

Absorbance was measured and percentage dyes removal was calculated by using formula:

$$\%\ \text{Dyes removal} = \frac{\text{Initial absorbance} - \text{Observed absorbance}}{\text{Initial absorbance}} \times 100 \quad \text{....... (Eq. 1)}$$

Results and Discussion

Effect of adsorbent dose and shaking speed on dyes removal: The percent (%) dyes removal at adsorbent doses of 2, 4, 6, 8, 10 g and at different shaking speed (100, 200, 300, 400, 500 rpm) was shown in Fig. 1d and (a) respectively. The effect of different adsorbent doses of rice husk on dyes removal at different shaking speed, contact time, pH and amount of dyes solution were also studied (Fig. 2). There was recorded 62 to 92% and 79 to 90% dyes removal at adsorbent doses of 2-10 g and with shaking speed of 100-500 rpms respectively. It was revealed that different quantities of adsorbent (rice husk) showed different percentage dyes removal from solution. The significant dyes removal of 91% was observed at 8 grams of adsorbent dose, while 93% of dyes removal was revealed at the shaking speed of 240 rpms. Small doses of rice husk did not prove to be an efficient in dyes removal in comparison to large doses. As more rice husk provide higher surface area and more adsorption sites availability to dyes. The dyes removal efficiency was increased due to the adsorbent dose which is supported by Khaled *et al*., (2009). They stated that higher doses increased the availability of large surface active sites and conglomeration of the adsorbent. The adsorbent concentration increased from 0.4 to 1.6 g dm^{-3} that increase the percentage dyes removal from 41% to 99%. Whereas decrease in the adsorption capacity at higher adsorbent concentration may be due to overlapping or partial aggregation of adsorption sites on the adsorbent surface (Akar *et al*., 2009).

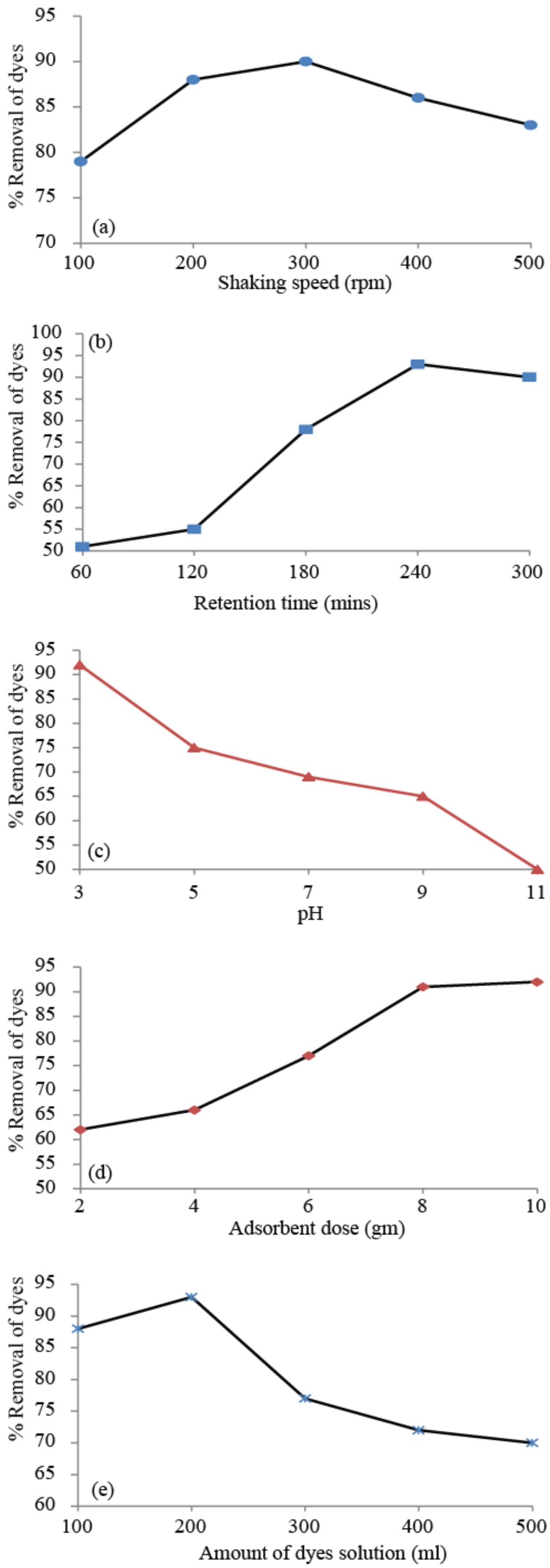

Fig. 1. Effect of (a) Shaking speed (b) Contact time/Retention time (c) pH (d) Adsorbent dose and (e) Amount of dyes solution on the percent (%) dyes removal.

Shaking speed is also significantly important for adsorbent dose. At higher shaking speed adsorbent doses seem to be more effective, but at much higher shaking speed (>500 rpms) reduces dyes removal at the adsorbent. This is due to the use of all the binding that becomes unavailable for adsorption. The insufficient dosage or overdosing would result in the poor performance in flocculation (Patel & Vashi, 2012).

Effect of contact/retention time on dyes removal: Contact time plays an important role in dyes removal. The minimum and maximum dyes removal efficiency was revealed in the range of 51 to 93% at retention time of 60 to 300 minutes as shown in Fig. 1b. Our results highlight significant 93% dyes removal when the retention time was maintained for 240 minutes. Percentage dyes removal is directly proportional to contact time. The dyes molecules intact for longer time with adsorbent surface because of their particles size, which provide more capacity for their bonding. Both are increased synergistically until equilibrium position reached. The relation between dye adsorption and retention time was studied to identify the dye removal. Dyes removal increased with increase in retention time (Amin, 2008). Our results clearly indicate that percentage dyes removal increases as the contact time increased at different adsorbent doses. Amin (2008) also studied an increase dyes removal as the contact time increased. The dyes removal efficiency decreased as equilibrium established that attributed to unavailability of active binding sites.

Our results are in concurrent with the studies of Khaled *et al*., (2009); Safa & Bhatti (2011). They studied that % dyes removal increased up to 3 hrs after that equilibrium position reached and there is no further increase noticed in the removal of dyes with increase in contact time. Akar *et al*., (2009) also studied the effect of agitation time on the RR198 dyes removal from aqueous solution and investigated dyes removal as with increase in time. It is the fact that in the start due to dyes molecules adsorption the rate of biosorption was rapid on the upper surface of the biosorbent. Demirbas (2009) also showed similar results for retention time with different charcoal adsorbents from agricultural residues (groundnut shells, bagasses, pea shells, wheat straw and tea leaves).

Effect of pH on dyes removal: The effect of different pH on dyes removal was shown in Fig. 1c. The % dyes removal was studied at different pH of 3.0 to 11.0. The minimum and maximum dyes removal efficiency of 50 and 95% was observed at 11.0 and pH 3.0 respectively. Least dyes removal was recorded at all pH except PH 3.0. Hence pH 3.0 was adopted as the optimum pH for further studies. Our results are also concurrent with the study of Isa *et al*., (2007); Khaled *et al*., (2009). They studied that acidic pH is favorable for dyes removal. Isa *et al*., (2007) noted maximum dyes removal (about 99%) at pH 2.0 and Khaled *et al*., (2009) observed 93.5 and 72.5% dyes removal at pH 2.0 and 3.0 respectively. They observed that dyes removal decreased as the pH moved from acidic to basic (4.0 to 12.0 pH) because in alkaline solution OH^- ions present. These ions are in competition with dye anions for adsorption sites. While in acidic pH, the increased H^+ ions revealed as the number of positively charged sites increased.

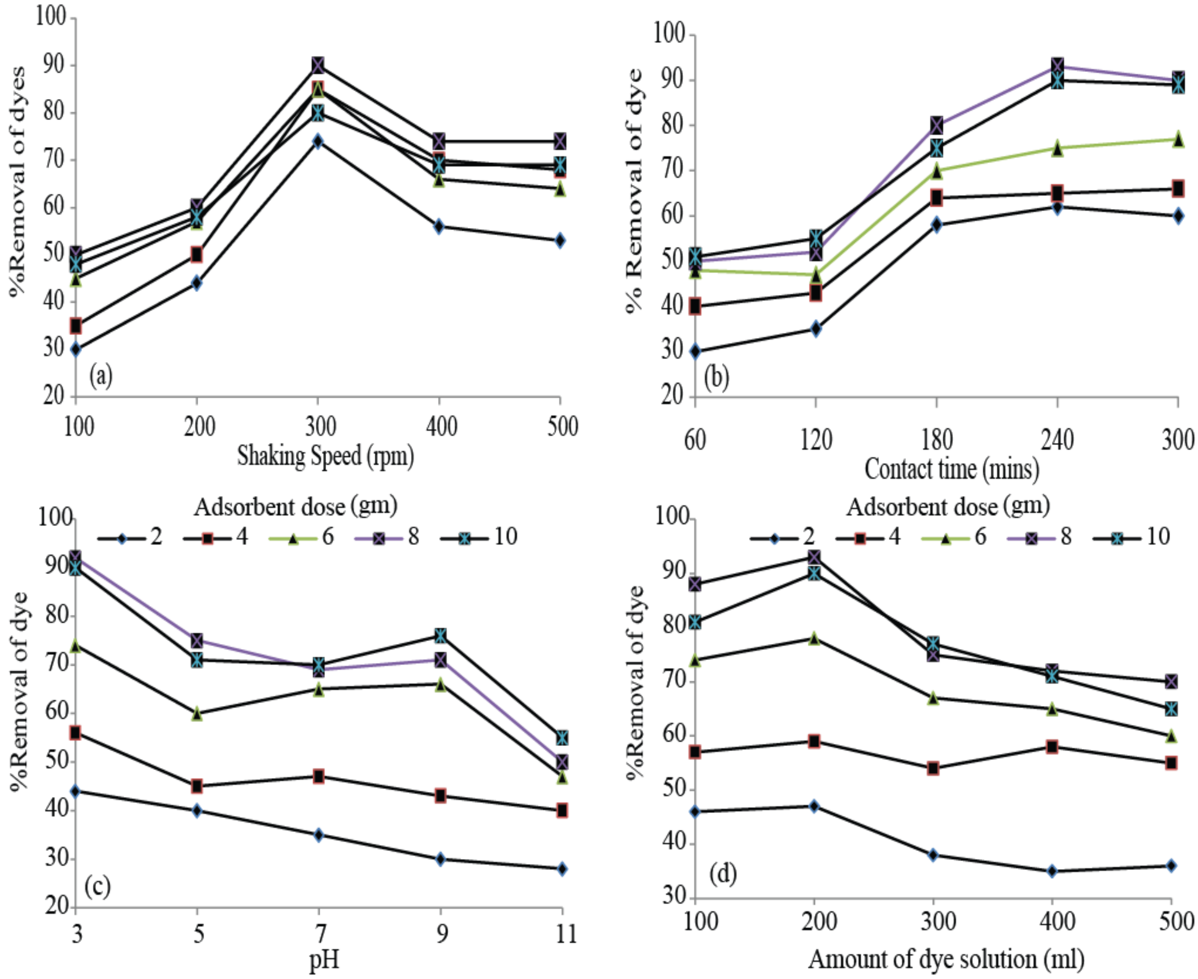

Fig. 2. Effect of different adsorbent dose of rice husk on dyes removal at (a) Shaking speed (b) Contact time (c) pH (d) Amount of dyes solution.

Safa & Batti (2011) also observed that maximum biosorption of Direct Red-31 and Direct Orange-26 was observed at pH 2.0 and 3.0, respectively. At lower pH the positively charged appear on the biosorbent surface and electrostatic attraction are created between the charged negatively anionic dyes and charge positively biomass (Khaled *et al*., 2009). However at higher pH (basic pH) hydro oxyle group adsorption process decreases due to anionic dyes competition at binding sites (Arami *et al*., 2006; Khaled *et al*., 2009). Ardejani *et al*., (2008) also concluded that pH increased from 2.0 to 12.0 as the adsorption capacity decreased from 20.5 to 18.8 mg/g.

Effect of amount of dyes solution on dyes removal: The effect of amount of dyes solution with percentage dyes removal was studied (Fig. 1e). The percentage dyes removal was in the range of 70 to 93% for the amount of dyes solution (100 to 500 ml). The maximum and efficient dyes removal was recorded 93% at 200 ml dyes concentration. Amin (2008) reported that the percent dyes removal decreased from 100 to 72, 98 to 70 and 90 to 58 as the initial dyes concentration increased from 10 to 90 ppm. Khaled *et al*., (2009) investigated that at different initial concentrations of dye DNB-106 (50, 75, 100, 125 and 150mg l^{-1}), the percentage removal efficiency was decreased as the initial dyes concentration increased in the solution. As amount of dyes increased, the available adsorption sites are readily deceased. Our results also reflect such high percentage dyes removal at initial dyes concentration but the dyes removal efficiency was decreased at the higher concentration as shown in fig 1 (e) and fig 2 (d). This may be due to the active site availability and increase in driving force of the gradient concentration as the initial dyes concentration increased (Safa & Bhatti, 2011).

Luo *et al*., (2011) showed that high removal efficiencies of water soluble acid dyes are at low concentrations (50 and 100 mg/L). Removal efficiencies of five kinds of water-soluble acid dyes applying 1-MA-3-MI-Br-mag-MIPs are almost 100%. The efficiencies declines as the acid dyes concentration become increased. Our study also reflects such results that lower amount of dyes concentrations (100-200 ml) showed 88 to 93% dyes removal. Safa & Batti (2011); Bullet (2007) also demonstrated that initial dyes concentration increases from 25 to 125 mg/g and 50 to 250 mg/L respectively as the amount of dye sorbed on the biomass surface.

Conclusions

Rice husk has been proved to be an efficient dyes removal from the impregnated cotton wastes and can be implemented on large scale. It has an extra advantage to eliminate the biological waste (rice husk) generated from rice husking mills because Pakistan is the largest rice producing country. The process of optimization concluded that efficient dyes removal was obtained at different optimized factors (Contact time, pH, Shaking speed, adsorption dose and amount of dyes solution). The maximum percentage dyes removal was ensured up to 93%. There is also a dire need to devise and implement standards related to dyes and levy charges on polluters. Dyes removal directly by rice husk from cotton wastes will ultimately result in environmental improvement, green production and sustainable development.

References

Akar, S.T. A.S. Özcan, T. Akar, A. Özcan and Z. Kaynak. 2009. Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste. *Desalination*, 249: 757-761.

Amin, N.K. 2008. Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. *Desalination*, 223: 152-161.

Arami, M., N.Y. Limaee, N.M. Mahmoodi and N.S. Tabrizi. 2006. Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull. *J. Hazard. Mater*., 135: 171-179.

Ardejani, F.D., K. Badii, N.Y. Limaee, S.Z. Shafaei and A. Mirhabibi. 2008. Adsorption of Direct Red 80 dye from aqueous solution onto almond shells: Effect of pH, initial concentration and shell type. *J. Hazard. Mater*., 151: 730-737.

Bulut, Y. N. Gozubenli and H. Aydin. 2007. Equilibrium and kinetics studies for adsorption of direct blue 71 from aqueous solution by wheat shells. *J. Hazard. Mater.,* 144: 300-306.

Crini, G. 2006. Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour. Technol*., 97: 1061-1085.

Demirbas, A. 2009. Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. *J. Hazard. Mater*., 16: 1-9.

Gong, R., Y. Sun, J. Chen, H. Liu and C. Yang. 2005. Effect of chemical modification on dye adsorption capacity of peanut hul. *Dyes Pigm*., 67: 175-181.

Isa, M.H., L.S. Lang, F.A. Asaari, H.A. Aziz, N. Azam Ramli and J.P.A. Dhas. 2007. Low cost removal of disperse dyes from aqueous solution using palm ash. *Dyes Pigm*., 74: 446-453.

Khaled, A., A.E. Nemr, A. El-Sikaily and O. Abdelwahab. 2009. Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: Adsorption isotherm and kinetic studies. *J. Hazard. Mater*., 165: 100-110.

Khan, M.Y., H.N. Asghar, M.U. Jamshaid, M. J. Akhtar and Z.A. Zahir.2013. Effect of microbial inoculation on wheat growth and phyto-stabilaztion of chromium contaminated soil. *Pak. J. Bot*., 45(S1): 27-34.

Luo, X., Y. Zhan, Y. Huang, L. Yang, X. Tu and S. Luo. 2011. Removal of water-soluble acid dyes from water environment using a novel magnetic molecularly imprinted polymer. *J. Hazard. Mater*., 187: 274-282.

Patel, H. and R. Vashi. 2012. Removal of Congo Red dye from its aqueous solution using natural coagulants. *J. Saud. Chem. Soc*., 16: 131-136.

Qadir, A., R.N. Malik and S.Z. Husain. 2008. Spatio-temporal variations in water quality of Nullah Aik-tributary of the river Chenab, Pakistan, *Environ. Monit. Assess*., 140: 43-59.

Safa, Y. and H.N. Bhatti. 2011. Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. *Desalination*, 272: 313-322.

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