Potential of Polymeric Materials (Microcrystalline Cellulose and Cotton Fibers) for the Removal of Anionic Dye from Textile Wastewater through Solid Phase Extraction

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Abstract: Alizarin red S dye is frequently used in textile industry and thus present in large quantities in out-drained industrial effluents, which pollute the sources of fresh water, by hindering the light and affecting the aquatic flora and fauna. Such water when used in irrigation purposes later causes threats for human health and animals life. In this work the dye has been effectively removed by using two polymeric materials i.e. microcrystalline cellulose and cotton fiber by solid phase extraction. Various concerned physical parameters were optimized for maximum adsorption through batch experiments. Kinetics of the adsorption process, thermodynamic studies, isotherm studies and desorption of the dye have also been studied. Q_{max} values for cotton and microcrystalline cellulose come out to be 6.612 mg/g and 5.573mg/g. Further this extraction proved to be spontaneous and endothermic in nature.

Keywords: Alizarin red S, Solid phase extraction, Wastewater treatment, Polymeric materials.

INTRODUCTION

In last few decades, one of the major problems resulted by the rapid technological and industrial developments in various countries, is pollution of fresh water resources. Especially in developing and under developed countries, due to not strict control of concerned government agencies, industries discharge their toxic effluents into lakes, rivers and streams and pollute even underground fresh water aquifers. In some countries textile is one of the major contributors for polluting the streams with dyes and other chemical pollutants. More than ten thousands types of synthetic toxic dyes are being poured by textile mills in fresh water streams around the world (Yagub, Sen *et al*. 2014). Synthetic dyes usually have complex aromatic structures, which make them stable and difficult to decompose. In addition to textile, dyes are used in a number of other industries like paper, plastic, leather, ceramic, cosmetic, ink, and food processing, etc. Dyes can be classified into different lasses such as acidic, basic, neutral, azo, dispersible, direct and reactive dyes (Bharathi and Ramesh 2013). Synthetic dyes as major class of pollutants and are responsible for making imbalances in aquatic ecosystems. Textile industries release huge quantities of dye-containing wastewater into water reservoirs because they use large quantities of water for dying process. The dyes released into rivers and streams are not only toxic for human beings but impart their toxicity to all types of aquatic life and disturb the ecosystems. These dyes are recalcitrant molecules, toxic to microorganisms and mammalian cells, mutagenic to rodents.

Alizarin red S is an important industrial dye which is also known as 2-Anthraquinonesulfonic acid; 1,2-dihydroxy-9,10-anthra-quinonesulfonic acid sodium salt; ARS and Alias Mordant Red 3. This dye produces purple and red colored solution depending upon pH (Roopaei *et al.,* 2014). Alizarin Red S is a water soluble and anionic dye, which is extensively used in industrial sector. Alizarin red S is a derivative of alizarin, which is a natural coloured substance extracted from the roots of *Rubiatinctorum* also known as madder and belongs to the family *Rubiaceae*. Alizarin red S can be synthesized by the sulfonation of alizarin (Ghaedi *et al.,* 2012).

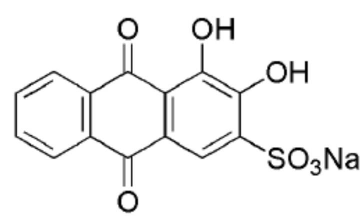

Figure 1: Structure of Alizarin Red S.

Other than used in textile as dye Alizarin red S is also used as acid-base indicator, in stain microscopy and in determination of fluorine (Abou-Gamra, 2014). The dye is also utilized to stain biological specimens such as small invertebrate embryos and mineralized bones in vertebrate groups. Alizarin red S is stored

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away from humidity and heat because it is a strong oxidizing agent. It is a non-biodegradable and chemically stable compound hence it cannot be fully degraded by conventional degradation processes. It is highly stable and almost unaffected by degradation process due to its structure that offers high optical, physicochemical and thermal stability (Machado *et al.,* 2016). Alizarin red S cannot be degraded easily because of its complex arrangement of aromatic rings; hence it turns noxious and a potential pollutant for the aquatic life and biota.

Generally dyes persist for a long time in aquatic systems due to slow degradation of their aromatic rings. This persistency leads to the higher pH values, low penetration of sunlight and higher value of TDS. The use of water containing even trace quantities of alizarin red S causes a number of harmful effects including malfunctioning of lungs, gastritis, painful micturition, severe headache and methemoglobinemia (Sujitha & Ravindhranath, 2016). It can be a potential source of eye and skin irritation, cytotoxicity, carcinogenicity, genotoxicity and toxicity of dye to freshwater organisms (Sabnis, 2008). In conventional treatment plants water is usually treated through anaerobic processes, which may convert the dyes into carcinogenic aromatic amines. This indicates the inadequacy of various treatment methods for removing dyes from the water. Depending upon the nature of the pollutant present, a number of physical, chemical and electrochemical methods are being employed to treat the wastewater. But most of the methods are expensive, time consuming, prone to residual effects and need sophisticated processing. Solid phase adsorption on a suitable adsorbent is however a simple, low-cost and effective method for removing the pollutants from water. Adsorption is especially an efficient method of detoxification of water from dyes. Various biological materials, composites of plant materials, and bio-water material are used for the removal of dyes from wastewater so far (Rehman, Mahmud *et al*. 2018).

Polymeric adsorbents are very distinctive class of adsorbents with maximum surface area; fine pore structure and greater adsorption capacity. These adsorbent materials are cheaper, easily available, and environmentally safer. Polymeric materials, due to their elastic nature, resistance to microbial attack, mechanical and thermal resistance, has been extensively used for removal of various pollutants (Torgut & Demirelli*.,* 2018). Natural or modified cellulosic material has also been used for the adsorption removal of various heavy metals. The adsorption potential of cotton, a natural polymeric material, has been studied for the removal of lead (II), zinc (II), copper (II) and cadmium (II) (Paulino*et al.,* 2014) and of polycyclic aromatic hydrocarbon (Wang *et al.,* 2014). In another study fluoride has also been removed by using iron (III) loaded cotton fiber (Zhao *et al.,* 2008).

EXPERIMENTAL WORK

Adsorbents

Two adsorbents; microcrystalline cellulose and cotton fibers were employed in this work. Both adsorbents were purchased from local market. Cotton fibers were thoroughly washed with distilled water and dried in oven till free from moisture.

Material / Reagents Used

Alizarin red S dye was obtained from Sigma Aldrich. Sodium hydroxide and sodium carbonate and hydrochloric acid used for the desorption studies and pH adjustment were of Merck Company. All the glassware used in this work was of Pyrex, Germany.

Standard Alizarin Red S Solution

One gram of alizarin red S was accurately weighed and dissolved in distilled water in a 1000 ml flask. When dye was completely dissolved by shaking well the volume was made up to the mark. This standard solution, 1000 ppm, was further diluted to prepare working standard solutions.

Procedure for Estimation of Alizarin Red S

Absorption of Alizarin red S at 423 was used for its estimation. A Spectrophotometer was used for this purpose. The same procedure was performed after each parameter optimization experiment, kinetics, and isothermal and thermodynamic studies. Standard alizarin solutions ranging from 5 to 35 ppm were used for the preparation of calibration line. After each experiment of adsorption of alizarin by the adsorbents, the alizarin solution was filtered and its absorption was measured. The remaining alizarin content was estimated by calibration graph.

Optimization of Parameters

In order to conduct the adsorption studies for alizarin red S, the effect of the following parameters were investigated.

Time of Contact

To check the effect of time on the adsorption process the contact time was varied from 5 to 70 minutes. This experiment was performed by shaking 0.2g of each adsorbent with 50mL of 25ppm dye solution at 150rpm shaking speed for different intervals of time at room temperature. All the samples were shaken keeping all the parameters constant except time.

Agitation Speed

Optimization of this parameter is based upon the fact that better contact of adsorbate with adsorbent results in the better adsorption of dye over adsorbent surface. Shaking speed, also called 'agitation speed', was studied with 0.2g of adsorbent in 50mL of 25ppm dye solution. Agitation speed was varied from 50 to 450rpm at optimized conditions of time of contact at room temperature.

Adsorbent Dose

Adsorption is generally based upon the fact that more adsorbate can be removed from aqueous medium by increasing the adsorbing sites. By increasing the adsorbent dose the number of adsorbing sites also increases. This parameter is optimized at room temperature by varying the adsorbent dose from 0.2 to 2.0g. 50mL of 25ppm dye solution was used at optimum conditions of time of contact and shaking speed.

pH of Solution

Quality of adsorption process is dependent upon this sensitive parameter. The pH value was optimized by shaking 50mL of 25ppm dye solution with optimum adsorbent dose, time of contact and shaking speed. pH was varied from 3 to11 in order to study the behavior of dye in acidic and basic medium. pH of the solution was adjusted by using 0.1M sodium hydroxide and 0.1M hydrochloric acid solution.

Temperature

Optimization of temperature was proceeded by varying the temperature of the solution from 10°C to 60°C using 50mL of 25ppm dye solution. Rest of the shaking conditions contact time, agitation speed, adsorbent dose and pH were kept at optimum values found in previous experiments.

Desorption

Desorption studies were conducted to check the regeneration of adsorbent which in turns favors its applicability, usability on large scale and environment friendly nature. Desorption study was carried out using 0.1M sodium hydroxide and 0.1M sodium carbonate. Adsorbents dose 1g were added in 50mL of the desorbing solution and agitated at 100rpm for 30 minutes.

Isothermal Study for Alizarin red S Removal

Adsorption mechanism was explored by conducting the isothermal, kinetics and thermodynamics study of the adsorption process for Alizarin red S on the selected adsorbents. For isothermal studies adsorption (%) for each adsorbent was calculated at any instant of time using equation 1.

$$\boldsymbol{Adsorption}\ (\%) = \frac{C_{\circ} - C_e}{C_{\circ}} \times 100 \quad (1)$$

'C_e' and '$C_{\circ}$' are the concentrations of alizarin before and after adsorption respectively. Three isothermal models; Langmuir, Freundlich and Temkin were used for exploring the adsorption mechanism of dye on polymeric adsorbents. Langmuir adsorption isotherm was studied using the equation 2.

$$\frac{1}{q} = \frac{1}{bq_m c_e} + \frac{1}{q_m} \quad (2)$$

Linearity of the plot between 1/q vs. $1/C_e$ revealed the applicability of the adsorption model. Favorability of the adsorption process was revealed by determining the dimensionless factor 'R_L' using equation 3.

$$R_L = \frac{1}{(1 + bCe)} \quad (3)$$

Freundlich adsorption model was studied to investigate the heterogeneous nature of adsorption process using equation 4.

$$logq_e = logK_f + \frac{1}{n} logC_e \quad (4)$$

Linear plot of 'log q' vs. 'log C_e' indicates the applicability of Freundlich adsorption model. Freundlich constant 'n' shows the quality of adsorption.

Third adsorption model that was applied to the dye adsorption was Temkin adsorption isotherm model using equation 5 that deals with the uniform distribution of energy throughout the adsorbent surface.

$$q = B_T\ InC_e + B_T\ InK_T \quad (5)$$

Linear plot of 'q' vs. 'ln C_e' reveals the applicability of this model. Temkin constant B_T gives information about the nature of interaction between adsorbent and the alizarin dye.

Kinetics Study for Alizarin red S Removal

Pseudo first and pseudo second order kinetics models are used for studying the kinetic behavior of alizarin adsorption process using equation 6 and 7 respectively.

$$log(q_e - q_t) = log q_e - \left\{\frac{k_1}{2.303}\right\}t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \left\{\frac{1}{q_e}\right\}t \quad (7)$$

Value of regression coefficient (R^2) in case of plotting a graph between log (q_e-q_t)' vs. 't' is helpful in concluding the suitable applicability of pseudo first order kinetics model. Whereas, in case of pseudo second order kinetics model linearity of the plot between 't/q_t' vs. 't' showed the suitability of the model for alizarin red S adsorption.

Thermodynamic Study for Alizarin red S Removal

Enthalpy (ΔHº) and entropy (ΔSº) of the adsorption process were calculated by the regression analysis of the linear plot of ln K_D vs. 1/T. Thermodynamic parameter Gibbs free energy (ΔGº) was then calculated using equation 9.

$$\Delta G° = \Delta H° - T\Delta S° \quad (9)$$

$$\ln K = -(\Delta H°/RT) + \Delta S°/R \quad (10)$$

Negative values of enthalpy and Gibbs free energy reveal that adsorption is exothermic and spontaneous in nature. Whereas, the positive value of entropy reveals the randomness in the system due to the interaction between alizarin and the adsorbent.

RESULTS AND DISCUSSION

Alizarin red S is an anionic dye that is frequently employed in the dyeing units of textile industry. Dyes are the class of organic pollutants that are carcinogenic and mutagenic in nature and in most cases non-biodegradable. They cause a serious health risk not only for human beings but also for aquatic life. They also result a physical hindrance to sun light to reach inside the water bodies. Removal of such pollutants from water bodies is needed to lower health risks and to save aquatic biota. But in under developed countries where the operational cost of any project is the deciding parameter, it is required to use such low-cast methodology that can be used by ordinary people at large scale for water purification. Adsorption is one of the cheap water detoxification technique in which use of indigenous materials makes it even more cheaper. In present work, alizarin red S was removed from aqueous media by solid phase extraction using two different adsorbents. These adsorbents belong to one category *i.e*, polymeric. Such study is always found to be influenced by two main factors: Adsorbents characteristics and Operational parameters. The results obtained from the characterization and optimization of the parameters are discussed as follows.

Characterization of Adsorbent

Selected adsorbents for the study, microcrystalline cellulose and cotton fiber, were characterized before and after adsorption experimentation by spectroscopic techniques including scanning electron micrographs and Fourier transform infrared spectroscopy.

S.E.M imaging/ EDX of the Adsorbents after Alizarin red S Adsorption

Scanning electron microscopy is a very powerful technique now a days to examine closely the surface structure of a substance. It has been used for exploring the surface of both the polymeric materials before and after adsorption of the dye. Change in the surface morphology is a clear indication of adsorption of dye on the surface of polymeric materials. ARS adsorbed adsorbent surface was coated with gold through gold sputter by applying accelerating voltage of 15kV. S.E.M micrographs of adsorbents before adsorption are shown in Figure **2**.

S.E.M analysis of the samples revealed a clear change in the surface morphology of the polymeric adsorbents. This reveals that raw form of all the adsorbents was suitable for the adsorption of ARS on the surface due to which alizarin red S interacted well on the surface and caused a visible change in the surface morphology of the adsorbents as shown in Figure **3**

FTIR ANALYSIS

a) Cellulose

FT-IR spectra of cellulose showed absorption bands at 3333.63, 2891.77, 1365.78, 1333.77, 1316.74, 1203.84, 1105.56, 1054.36, 1029.32, 663.54 and

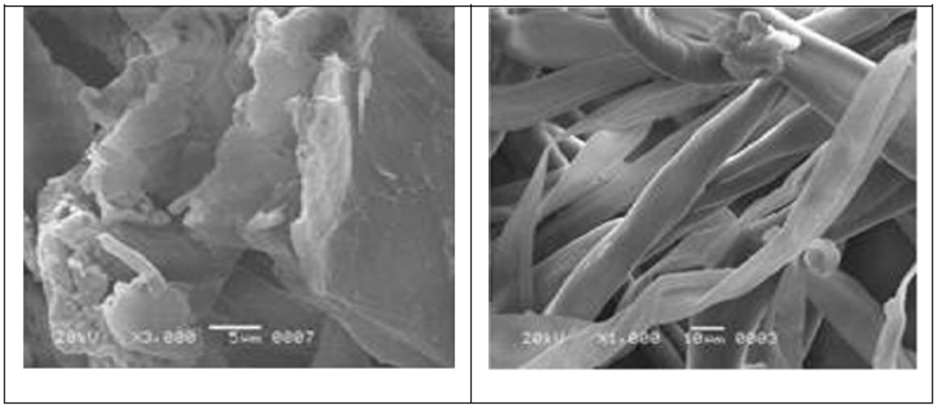

Figure 2: S.E.M. image of; **a** (*Raw cellulose*), **b** (*Raw cotton*).

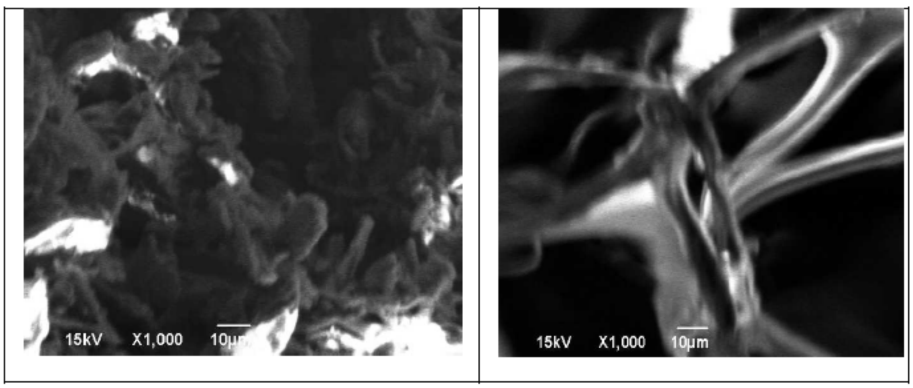

Figure 3: S.E.M. image of; **a** (ARS adsorbed cellulose), **b** (ARS adsorbed cotton).

657.55 cm^{-1}. The band at 3333.63 cm^{-1} corresponds to H-bonded O–H alcohols, phenols. The band at 2891.77 cm^{-1} is characteristic of C–H stretching vibrations whereas the bands at 1203.84, 1105.56, 1054.36 and 1029.32 cm^{-1} correspond toC–O stretching (Pavia, 2001).

b) Cotton

FT-IR spectra of cotton showed absorption bands at 3340, 3296, 2892, 1316, 1205, 1152, 1109, 1056 and 1031 cm^{-1}. The bands 3340 and 3296cm^{-1} correspond to H-bonded O–H of alcoholic and phenolic groups. The peak at 2892$cm^{-1}$is the characteristic peak of C–H

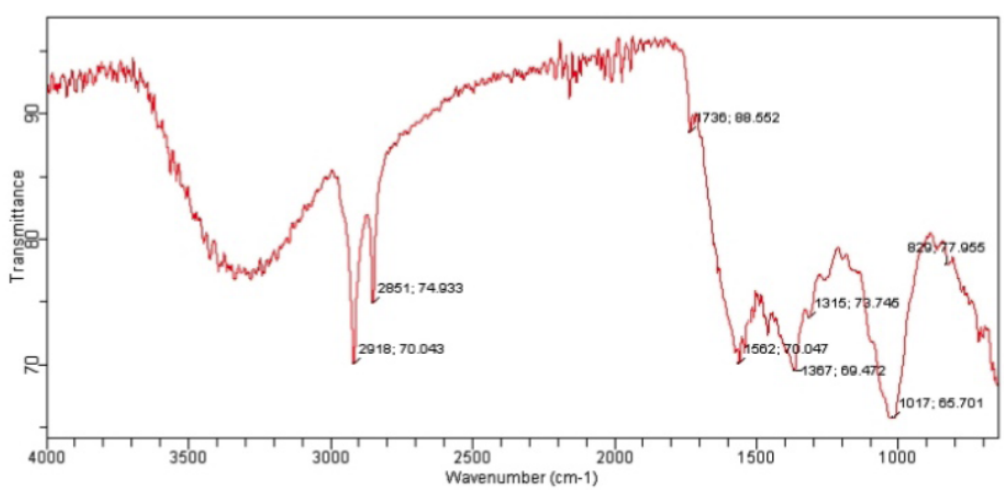

Figure 4: FT-IR spectrographs of cellulose.

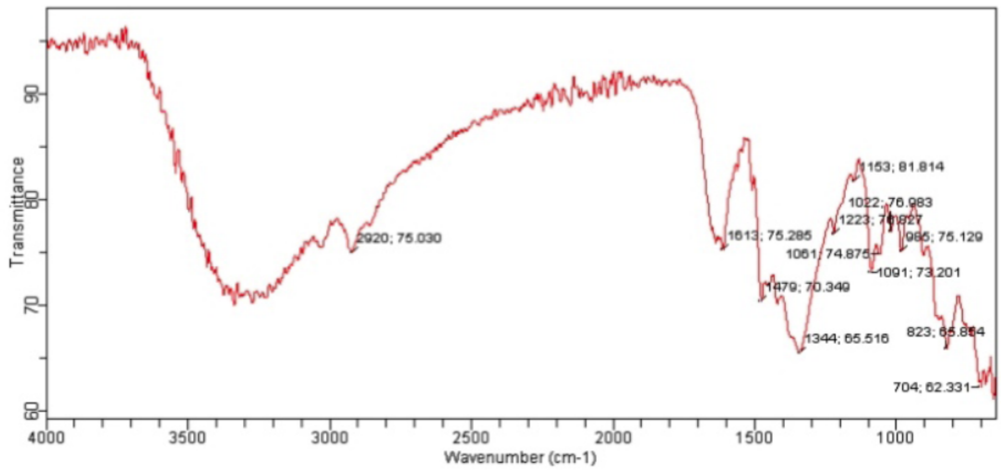

Figure 5: FT-IR spectrographs of cotton.

stretching vibrations in alkanes whereas the one at 1316cm^{-1} corresponds to C-N stretching vibrations for amines. The peaks at frequencies 1205, 1152, 1109, 1056, 1031 cm^{-1} correspond to C–O stretching (Pavia, 2001).

PARAMETERS OPTIMIZATION

Effect of Time of Contact

In case of polymeric adsorbents highest removal efficiency (98.32%) was shown by cellulose after 35 minutes of contact time as graphically represented in Figure **6**.

The adsorption of alizarin increased in the beginning due to the availability of greater number of adsorption sites. With the passage of time alizarin tends to cover adsorbent surface thereby reducing the removal efficiency gradually. Aggregation of bigger dye molecule tends to hinder the further adsorption with the passage of time on the adsorbent surface as a result of which a general reduction of removal efficiency with the passage of time was observed in both cases.

Effect of Agitation Speed

Both adsorbents showed almost comparable affinity for alizarin red S as far as speed of agitation was concerned as shown in Figure **7**. Cellulose as well as cotton fiber have been found to show maximum removal efficiency at 150 rpm. Further increase in the agitation speed resulted in the decreased adsorption of dye.

Percent removal of alizarin increased in start and after equilibrium was attained no remarkable increase in removal efficiency was observed rather removal efficiency tends to decrease. Contact between dye present in the solution and surface of the adsorbent

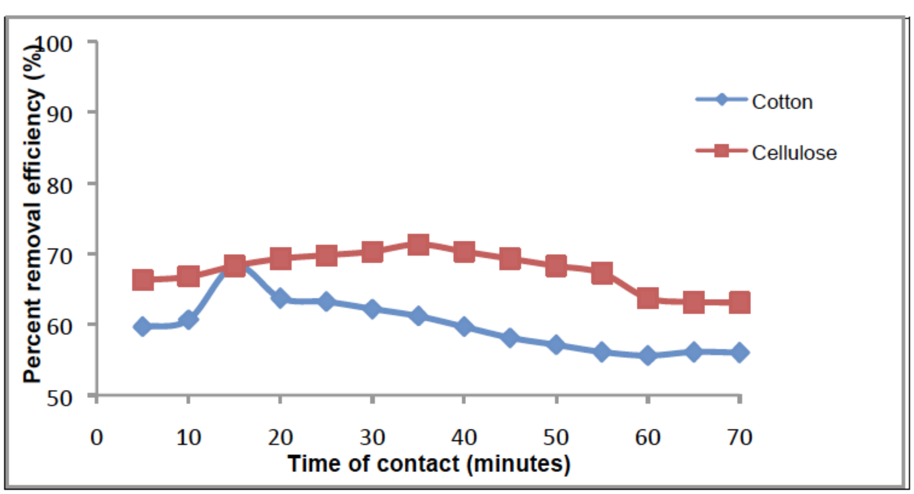

Figure 6: Effect of contact time on alizarin red S adsorption using polymeric adsorbents.

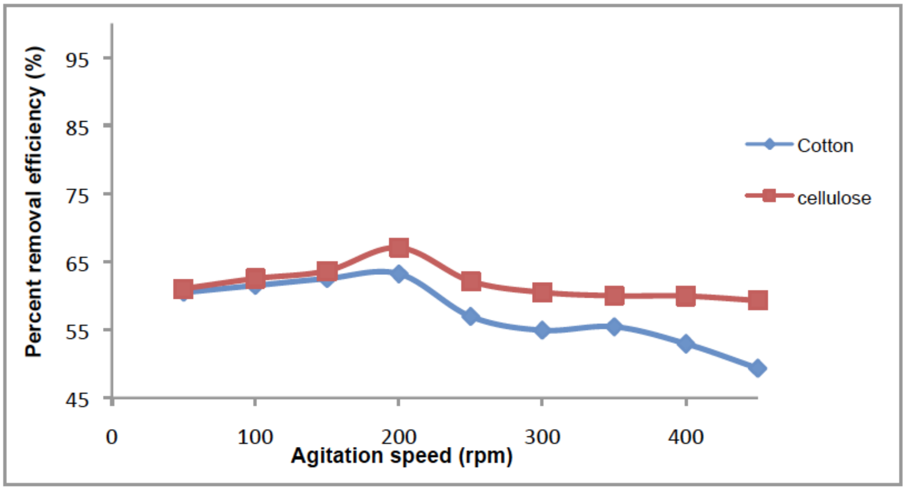

Figure 7: Effect of agitation speed on alizarin red S adsorption using polymeric adsorbents.

was affected by agitation speed. Agitation increases the external mass transfer coefficient that resulted in the increased adsorption of alizarin. As all the sites get filled further increase in agitation speed had negative impact on the adsorption because of availability of lesser time for interaction between adsorbent surface and alizarin in the solution. Lesser time to interact due to higher speed increased the chances of collision of molecules with adsorbent surface in such a way that the adsorbed ions might get detached from the adsorbent surface thereby resulting in a slight decrease in percentage removal of the dye.

Effect of Adsorbent Dose

Cellulose showed greater removal efficiency between both the polymeric adsorbents selected for study. Removal efficiency increased in the beginning and attained the maximum value with 0.6g of cellulose. The cotton fibers showed a marked maximum efficiency at 0.7g adsorbent dose. The results are graphically represented in Figure **8**.

It was revealed generally that by varying the adsorbent dose from 0.2 to 2.0g removal efficiency was found to increase for all the adsorbents up to a certain limit. This increase was attributed to the fact that by increasing the adsorbent dose the active sites available for alizarin adsorption increased accordingly. As the concentration of alizarin was kept constant; increasing the adsorbent dose increased the ratio of adsorbent to adsorbed alizarin. After reaching the maximum removal efficiency no further increase was observed even after increasing the dose. This might be due to the reason that with the constant alizarin concentration; initially plenty of dye was available for the active adsorption sites. When all the active sites were covered with dye further adsorption was hindered by the presence of

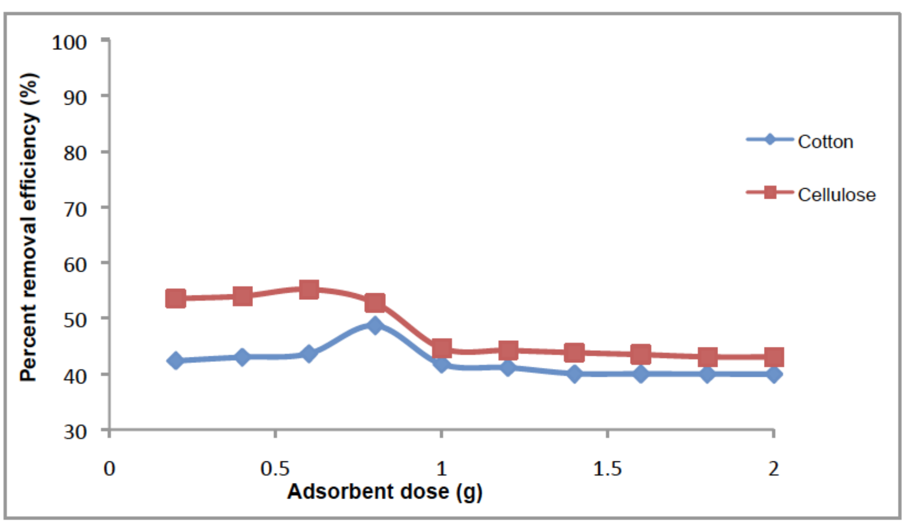

Figure 8: Effect of adsorbent dose on alizarin red S adsorption using polymeric adsorbents.

bulky dye molecules. As a result the percent removal nearly becomes constant after reaching a certain maximum value. Similar trends were observed in a previous work by using nano-composites of activated carbon (Fayazi *et al*., 2015).

Effect of pH of the Solution

In case of polymeric adsorbents, dye was effectively removed using Cotton and cellulose at pH 7. As the results reveal in Figure **9** no appreciable change has been found in adsorption by cotton fibers but a marked enhancement in adsorption was found in the case of microcrystalline cellulose. Results of pH effect on the adsorption for both the adsorbents are graphically represented in Figure **9**.

In fact pH is the major factor affecting the adsorption of alizarin red S on the adsorbent surface. Existence of alizarin in solution is highly dependent upon the pH of the solution as it effects the ionization of the dye. Another factor that affects the dye adsorption is the value of pH_{pzc} of the adsorbent. As the pH is lower than pH_{pzc} the surface of adsorbent will acquire the positive charge and when pH is higher than pH_{pzc} the surface of adsorbent will attain the negative charge. It means that surface of adsorbent can provide several types of direct or indirect, physical /chemical interactions to the monovalent and multivalent anions present in the solution. Direct interactions may result from the attraction between positive charge on adsorbent surface and negatively charged monovalent alizarin molecules that are predominantly present at

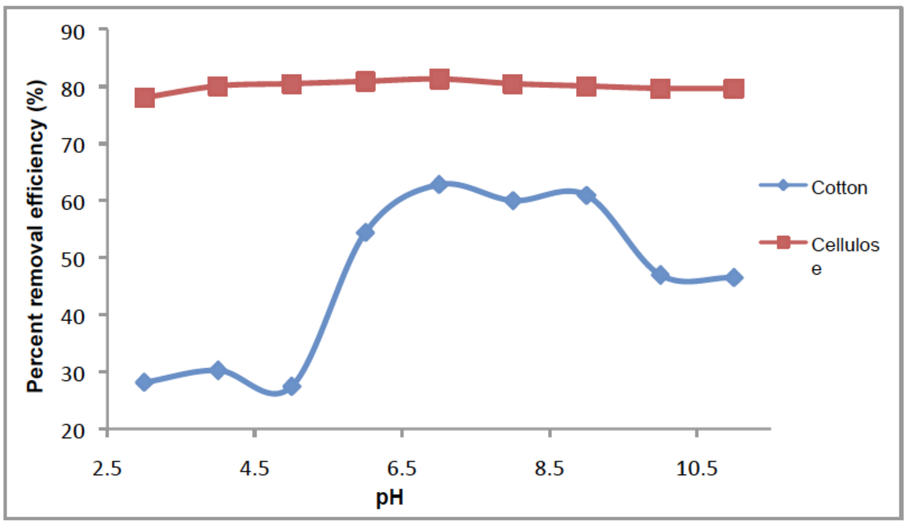

Figure 9: Effect of pH on alizarin red S adsorption using polymeric adsorbents.

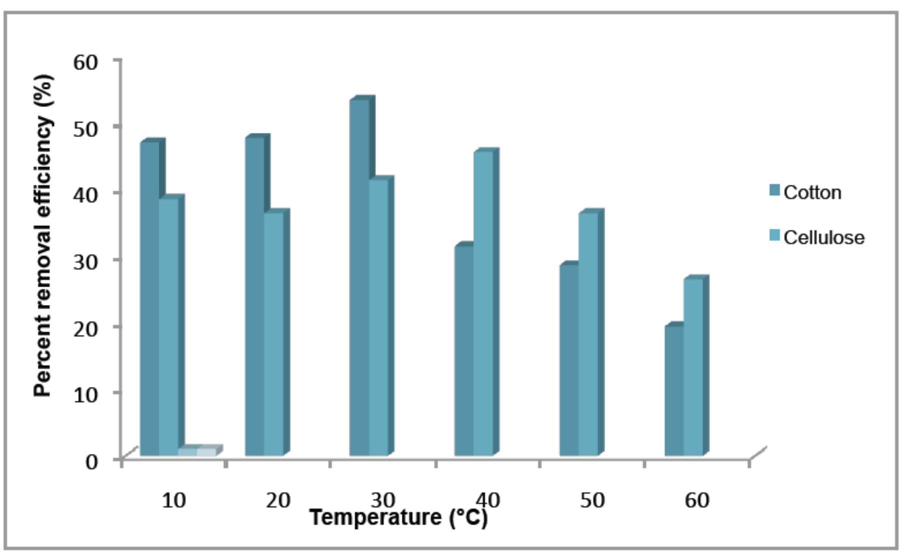

Figure 10: Effect of temperature on adsorption of alizarin red S using geological adsorbents.

lower pH. Increase in the pH of the solution (basic medium) result in the excess of negative charge on adsorbent surface, which reduced the removal efficiency in basic medium. Similar trends were observed with nano-composites of activated carbon when employed for alizarin red S removal by adsorption (Fu *et al*., 2011).

On the surface of cotton and cellulose various amines, carboxyl, lingo-cellulosic materials and alcoholic groups are present that may dissociate under the effect of solution pH and result in the better adsorption at neutral pH. This is in accordance with the previously found results (Mahvi *et al*., 2004).

Effect of Temperature

In case of polymeric adsorbents; effect of temperature on adsorption of alizarin red S was studied by varying the temperature from 10 to 60 °C keeping all the other parameters constant. The results are graphically represented in Figure **10**.

Temperature is the major factor responsible for the movement of the molecules and ionic species in the solution as well as the interaction of these species with the adsorbent surface. At room temperature (25 °C) molecular movements were effective enough for the better interaction of alizarin with adsorbent surface thereby resulting in better adsorption. Higher temperature was found to affect the adsorption process either by affecting the resultant interaction or by varying the solution concentration. Adsorption of alizarin generally increased with increasing temperature showing that better adsorption was observed at higher temperature. With increase in temperature the rate of diffusion of alizarin across the external boundary layer of adsorbent increased thereby decreasing the viscosity of solution. Evaporation may affect the concentration of the solution at higher temperature and was found to affect the results of adsorption study. Therefore, the effect of temperature was studied from 10 to 60 °C. Similar behavior was shown by other dyes as reported in literature (Longhinotti *et al*,. 1998: Tahir & Rauf, 2006: Iqbal & Ashiq, 2007).

Effect of Desorbing Reagent

Regeneration of the adsorbent is very important as it affirms its reusability and ecofriendly nature. Adsorbents can be re-employed for removal of toxic species after regeneration. Sodium hydroxide is found more effective in desorbing the alizarin red S from the selected adsorbents as compared to Sodium carbonate. This might be due to the fact that formation of sodium salt of dye facilitated desorption of alizarin from the adsorbent surface. In case of sodium hydroxide the counter ion is relatively smaller as compared to the carbonate ion, thereby facilitating the salt formation. Desorption results for the polymeric adsorbents are graphically represented in Figure **11**. Sodium hydroxide showed higher desorption results.

Isothermal Modeling for Alizarin Red S

Isothermal studies were conducted at the optimized conditions of time of contact, agitation speed, adsorbent dose and pH of the solution. Comparative isothermal parameters are shown in Table **1**.

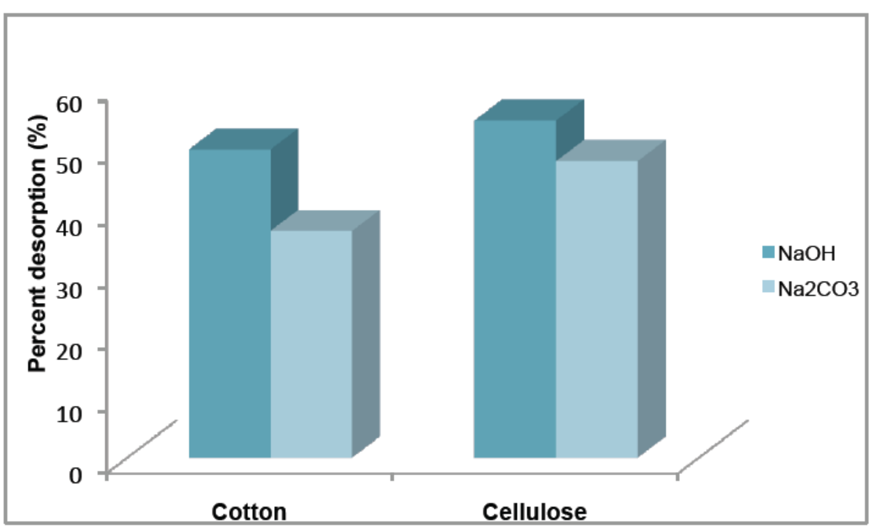

Figure 11: Effect of desorbing agent on alizarin adsorbed polymeric adsorbents.

Table 1: comparative Isothermal Parameters for Alizarin Removal using Polymeric Adsorbents

Adsorbent	Langmuir Isothermal Parameters				Freundlich Isothermal Parameters			Temkin Isothermal Parameters		
	R^2	Q_{max} (mg/g)	B (L/g)	R_L	R^2	n	K_f (mg/g)	R^2	B_T (kJ/mol)	K_T (L/mg)
Cotton	0.947	6.612	0.008	0.833	0.944	0.868	0.114	0.856	1.998	0.431
Cellulose	0.986	5.573	0.039	0.506	0.978	1.081	0.306	0.912	2.037	0.780

Value of regression coefficient (R^2) is close to unity in case of those adsorbents where Langmuir adsorption isotherm holds good to explain the adsorption of alizarin red S. it is also clearly suggested from the data that there are fixed number of adsorption sites uniformly distributed on adsorbent surface and alizarin has equal affinity towards adsorption sites with no lateral interaction among dye molecules. Moreover, the Q_{max} value is also indicative of the fact that among the polymeric adsorbents cotton fibers showed greater tendency for dye adsorption.

Value of this dimensionless constant is below 1 which suggested that adsorption of alizarin red S by the adsorbents selected for this study was favorable process and these adsorbents can be used for large scale removal of alizarin red S from waste water.

Multilayer adsorption on the heterogeneous surface of adsorbent was explored by applying the *Freundlich isotherm*. This multilayer adsorption can be further explained by the lateral interaction among the alizarin molecules. Non linearity of the system increased with the increased value of 'n' that is associated with the increased heterogeneity of the adsorbent surface. Value of 'n' from 2 to10 indicates the better adsorption whereas from 1 to 2 predicts good adsorption. Higher values of K_f indicated the effective bonding of dye on the adsorbent surface. Higher K_f values for alizarin showed that alizarin penetrated well in the heterogeneous adsorbent surface and was effectively removed by cellulose.

Temkin isotherm model explains the equal distribution of binding energies on the adsorbent surface. Value of 'B_T' below 8 revealed the weak interaction that can be interpreted as physiosorption. Such interactions were shown by both the adsorbents. Lower B_T values are indicative of the fact that adsorbents can easily be regenerated after desorption. Higher K_T values are indicative of the fact that stronger interactions are present between the adsorbent surface and alizarin dye. Comparison of the adsorption capacity of the adsorbents previously used for anionic dye removal and the adsorbent selected in the present study are represented in Table **2**.

Kinetic Study for Alizarin Red S Adsorption

Kinetics study showed the removal of alizarin red S as a function of time and data obtained is tabulated in Table **3**. The dependence of experimental data on time was investigated by applying pseudo first and pseudo second order kinetics models.

When maximum alizarin was adsorbed the adsorbent becomes saturated thereby revealing the adsorption capacity of each adsorbent for alizarin. Theoretical and experimental adsorption capacities represented as Q_t and Q_{exp} are shown in the Table **3**.

Table 2: Comparision of Adsorption Capacity of Adsorbent Previously used with Present Study

Adsorbents	Dyes	Q_{max} (mg/g)	References
Mustard Husk	Alizarin Red S	1.97	Gautam, R.K. *et al*., (2013)
Cynodon Dactylon	Alizarin Red S	16.32	Samusolomon, J. *et al.,* (2011)
Activated clay modified by iron oxide	Alizarin Red S	32.7	Fu,F. *et al*., (2011)
Raw chickpea husk	Alizarin Red S	5.853	Dar, A. *et al.,* (2017)
Zinc modified chickpea husk	Alizarin Red S	39.30	Dar, A. *et al*., (2017)
*Microcrystalline Cellulose	Alizarin Red S	5.573	Present study
*Cotton	Alizarin Red S	6.612	Present study

Table 3: Kinetic Study for Adsorption of Alizarin Red S

Adsorbent	Pseudo First order Kinetics Parameters			Pseudo Second Order Kinetics Parameters			Q_{exp} (mg/g)
	R^2	K_1 (min^{-1})	Q_t (mg/g)	R^2	K_2 (g/mg/min)	Q_t (mg/g)	
Cotton	0.0689	0.0007	1.248	0.9984	2.720	0.961	1.07
Cellulose	0.9879	0.0489	1.339	0.9998	0.907	1.504	1.49

Table 4: Thermo-Dynamical Parameters for Adsorption of Alizarin Red S

Adsorbents	Thermodynamics Parameters			
	R^2	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
Cotton	0.916	-0.420	-1.294	0.802
Cellulose	0.829	-0.467	1.429	0.175

Comparison of the regression coefficient (R^2) values showed that pseudo second order model is more in accordance with the data. In both cases the R^2 values for pseudo second order kinetics model are approaching unity. Theoretical and experimental adsorption capacity values were not in agreement with each other for pseudo first order kinetics model. Whereas, in the case of pseudo second order kinetics model theoretical and experimental adsorption capacity for alizarin were in accordance with each other which showed the better applicability of this model.

Thermodynamic Study for Alizarin Red S Adsorption

Negative values of ΔGº indicate the spontaneous nature and thermodynamic feasibility of adsorption of alizarin using all the adsorbents. Increased negative value of ΔGº with temperature indicates the increased alizarin removal at high temperature. Negative values of ΔHº revealed the exothermic nature of alizarin adsorption process, whereas the positive ΔHº values revealed endothermic nature of alizarin adsorption. For significant adsorption of alizarin the negative values of ΔGº must be accompanied with the negative values of ΔHº as shown in case of cotton. Positive values of ΔSº showed that when alizarin interacted with the adsorbent surface, this interaction imparted randomness to the system.

CONCLUSION

From the study conducted it has been concluded that use of polymeric material has proved to be very useful in eradicating the problem faced by contamination of fresh water sources with textile effluents. Mathematical modeling using isothermal kinetics and thermodynamics study revealed that monolayer adsorption pattern best explained the adsorption of dye onto polymeric surface. Pseudo second order kinetics model showed good data fit. Thermodynamics parameters revealed the spontaneous, endothermic nature of alizarin interaction with polymer surface. It is therefore recommended that theses polymeric material can be used for the dye removal at larger scale.

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