Comparative Removal of Congo Red Dye from Water by Adsorption on *Grewia asiatica* Leaves, *Raphanus sativus* Peels and Activated Charcoal

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Summary: Water treatment by adsorption methodology is being evolved in recent years. Various researchers are searching new adsorbents for water treatment which can replace activated charcoal. In the following study, the efficiency of removing Congo Red dye from water using two novel adsorbents, i.e. *Raphanus sativus* (Radish) peels and *Grewia asiatica* (Phalsa) leaves was evaluated and compared with activated charcoal. The adsorption process is carried out batch wise by using different concentrations of the aqueous dye solution with different adsorbent doses, agitation rate, varying contact time intervals, at a range of initial pH values and at different temperatures. Various chemicals were used for enhancing the adsorption capacity of adsorbents. The suitability of the adsorbent for using it is tested by fitting the adsorption data on Langmuir isotherm. The results showed that the Phalsa leaves powder is more effective adsorbent than Reddish peels for removing Congo Red dye from water. It can be used for removing Congo Red dye from waste water.

Keywords: *Raphanus sativus peels*, *Grewia asiatica leaves*, *activated charcoal*, *Congo Red dye*, *adsorption*, *Langmuir isotherm.*

Introduction

Waste water from the textile, cosmetics, printing, dying, food coloring and paper-making industries is polluted by dyes. These colored effluents can be mixed in surface water and ground water systems. Then they may also transfer to drinking water. In literature, almost 40,000 dyes and pigments are listed which consist of over 7000 diverse chemical structures. Most of them are completely resistant to biodegradation processes. More than 7×10^5 tones of dyes and pigments are produced annually worldwide. A lot of them are wasted during processing and manufacturing operations [1-3].

Waste water contains various kinds of synthetic dyestuffs. These dyes can be classified in three broad classes: anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes and vat dyes). Generally cationic dyes are more toxic and harmful than anionic dyes. The present research work describes the removal of Congo Red dye from water. It is an anionic diazo direct dye which contains $-NH_2$ and $-SO_3$ functional groups. It exists as brownish-red crystalline solid and is stable in air with a high solubility in water, i.e., 1.0 g/30 mL. Its IUPAC name is 1-napthalenesulfonic acid, 3,3-(4, 4-biphenylenebis (azo))bis(4-aminodisodium) salt. It is also called Direct Red-28 and Cotton Red. Its structural formula is given in Fig. 1 [4].

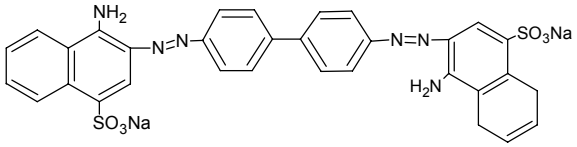

Fig. 1: Molecular structure of Congo Red dye.

The color of Congo Red changes from dark blue at pH 2.0 –4.0 to red to pH 12.0. However, the intensity of red color is different from the original red at pH 10.0 – 12.0. That's why it is usually employed as an indicator of pH, in the diagnosis of amyloidosis, histological stain for amyloid and as a laboratory aid in testing for free hydrochloric acid in gastric contents. It has a strong affinity to cellulose fibers and thus is employed in textile industries. It is a derivative of benzidine and napthoic acid. Its decomposition results in carcinogenic products. It is a mutagen and affects reproductive systems of living things. It acts as a skin, eye and gastrointestinal irritant. It impresses blood factors such as clotting and induces drowsiness and respiratory problems [5-7].

Dyes can cause skin irritation, cancer, allergic dermatitis and mutations. Therefore, it is necessary to remove the dye from waste water before it enters into fresh water stream. For this purpose,

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many methods, such as reverse osmosis, chemical oxidation, coagulation, flocculation and biological treatments have been developed for treating dye containing wastewater. Activated carbon has been widely used in wastewater treatment to remove organic and inorganic pollutants. Development of low cost alternative adsorbents has been the focus of recent researchers because of the high cost of activated carbon. A number of scientists have studied the feasibility of using low-cost substances for the removal of various dyes and pollutants from wastewaters. Several novel biomaterials have been employed as adsorbents. It has two main advantages. First is that activated carbon can be replaced with economical alternatives and secondly various waste products of agriculture related industries like food processing can be employed for this useful purpose in order to save money and also converting waste material into useable form [7, 8]. Such low cost adsorbents have found useful at least in laboratory scale for treatment of colored effluents in batch wise mode. Efforts are continued to adopt them on larger scale in continuous way.

Various adsorbents have been tried for removal of Congo Red dye from water like *Azadirachta indica* leaf powder, banana peels, orange peels, straw carbon, rice husk carbon, treated and untreated sunflower stalk, Penicillium, ground nut shell carbon, bamboo dust carbon, bagasse fly ash, bentonite, bottom ash, de-oiled soya, jute sticks and kaolins [9-21].

In the present research work *Grewia asiatica* (Phalsa) leaves and *Raphanus sativus* (Radish) peels are used as novel adsorbents for removing Congo Red dye from aqueous media. Their efficiency of removing dye is compared with activated charcoal. Phalsa (*Grewia asiatica* L., Tiliaceae) is a bushy plant, used as a folk medicine. It is a large, shaggy shrub or a small tree reaching four meter or more in height depending upon climatic conditions. The leaves are applied on skin eruptions and they are known to have antimicrobial action. The fresh leaves are used as animal fodder. Its fruit relieves inflammation and is used in respiratory, cardiac, and blood disorders, as well as for fever reduction. The infusion of the bark is given as a demulcent, febrifuge and for the treatment of diarrhea. The root bark is employed in treating rheumatism. The wood is yellowish-white in color, fine-grained, strong and flexible. It is used for archer's bows, shingles, spear handles and poles for carrying loads on the shoulders. Stems that are pruned serve as garden poles and for basket making. Radish (*Raphanus sativus var. longipinnatus*) has many varieties. It is oblong in shape, approximately 20 to 35 cm long and 5 to 10 cm in diameter. It is mostly used in salad and for decoration of cooked food in sub-continental areas [22-24].

Results and Discussion

Characterization of Adsorbents Surface

The first step was the characterization of adsorbents surface to confirm the presence of functional groups like -OH, -CO, -CHO, N-H, -CONH, -C=C- and -COOH that can be used for bonding with Congo Red dye during adsorption. For this purpose, all the adsorbents were characterized by FT-IR and the resulting characteristic vibration frequencies have been mentioned in Table-1. From Table-1, it is observed that the characteristic absorption bands of N-H, -CHO, -CO, and -NCO groups are present in the FT-IR spectra of *Raphanus sativus* peels (R.P), *Grewia asiatica* leaves (G.L) and activated charcoal (A.C), which are responsible for the adsorption of dye. Region below 1000 cm^{-1} corresponds to the complex interacting vibration. So it can not be used to represent any particular functional group (fingerprint region) [27].

Table-1: Characteristic FT-IR band absorption frequencies of adsorbents.

Adsorbent	Bond frequencies (cm^{-1})
Raphanus sativus Peels	**3291 (m), 2917 (w), 2354.3 (w), 1612 (m), 1241.6 (s),**
Grewia asiatica leaves	**3372.8 (m), 2916.2 (m), 1683.7 (m), 1620.9 (m), 1521.4 (s), 1158.8 (w)**
Activated Charcoal	**3784 (m), 2934 (s), 2361 (m), 1688 (s), 1564 (m), 1460 (w), 1289 (w)**

Where s= strong, m= medium and w= weak signal in FT-IR spectrum

Effect of Particle Size

To study the effect of particle size of adsorbents, different mesh sized *Raphanus sativus* peels (R.P), *Grewia asiatica* leaves (G.L) and activated charcoal (A.C) were used for adsorption. The results are shown in Fig. 2.

Maximum %age removal of dye is observed by using *Grewia asiatica* leaves of mesh size of 20-40 microns. It was found that adsorption rate decreases with increase in mesh size of adsorbents. The particle size decreases and surface area exposed for adsorption of dye increases as mesh size increases. This may be due to increase in the accessibility of the adsorbate to the pores of the adsorbents with the decrease in particle size [12-19, 25].

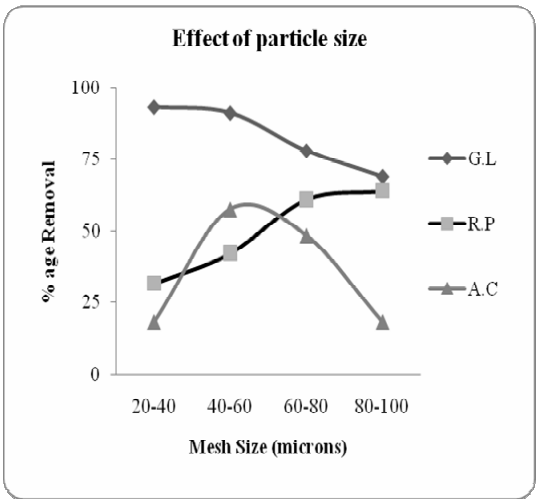

Fig. 2: Effect of particle size of Raphanus sativus peels (R.P), Grewia asiatica leaves (G.L) and activated charcoal (A.C) on %age removal of Congo Red dye from water.

Effect of Adsorbent Dose

The study of adsorbent dose for the removal of the dye from aqueous solution was carried out using *Raphanus sativus* peels (R.P), *Grewia asiatica* leaves (G.L) and activated charcoal (A.C) quantities ranging from 0.5 to 2.5 g. The %age of dye removal was attained for adsorbent dose of 0.5 g of *Grewia asiatica* leaves, 1.0 g of activated charcoal and 2.0 g of *Raphanus sativus* peels as shown in Fig. 3. For adsorbent quantities higher than these values, the dye removal decreases. Increase in the percentage of the dye removal with adsorbent masses was related to increase in the adsorbent surface areas, enhancing the number of adsorption sites available for adsorption as reported already in other cases [12-20, 26].

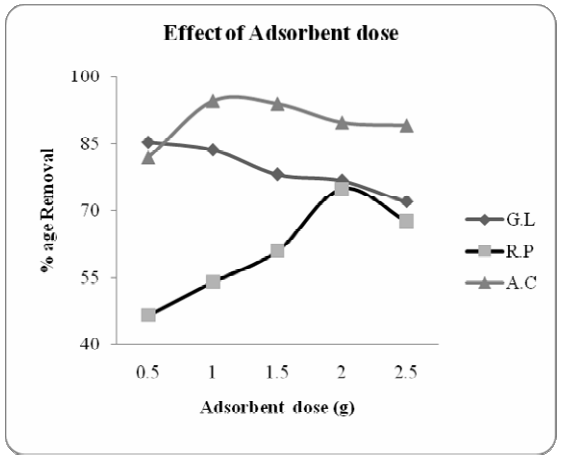

Fig. 3: Effect of adsorbent dose of Raphanus sativus peels (R.P), Grewia asiatica leaves (G.L) and activated charcoal (A.C) on %age removal of Congo Red dye from water.

Effect of Contact time

The effect of various contact intervals between *Raphanus sativus* peels (R.P), *Grewia asiatica* leaves (G.L) and activated charcoal (A.C) adsorbents and dye solution on adsorption was studied. The results are shown in Fig. 4. The maximum adsorption values were obtained when the contact time was 20, 30 and 40 minutes in case of *Raphanus sativus* peels, *Grewia asiatica* leaves and activated charcoal respectively. The maximum %age removal of dye by using *Grewia asiatica* leaves was 88.08 %, whereas 94.17 and 68.15 % using activated charcoal and *Raphanus sativus* peels respectively.

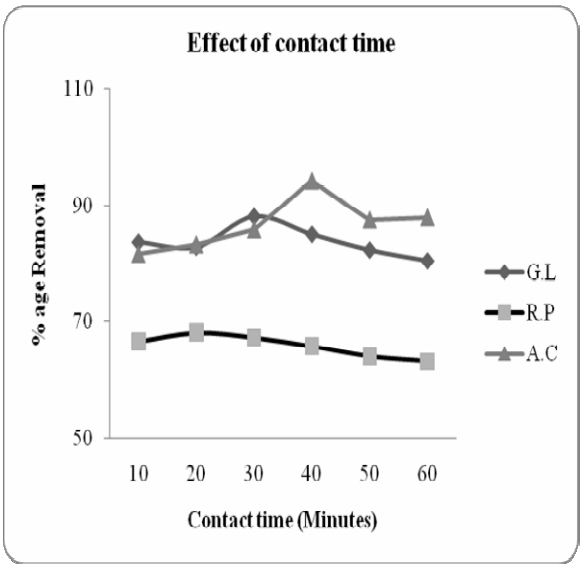

Fig.4: Effect of contact time of Raphanus sativus peels (R.P), Grewia asiatica leaves (G.L) and activated charcoal (A.C) with aqueous solution of dye on %age removal of Congo Red from water.

The results showed that activated charcoal can remove a large quantity of Congo Red dye. *Grewia asiatica* leaves are effective for adsorption, like activated charcoal adsorbent due to the availability of more adsorption sites. *Raphanus sativus* peels can adsorb a smaller quantity of dye in comparatively less time. They have less adsorption sites which are filled up in short interval of time. That's why, its adsorption capacity is less. The adsorption rates decreased to a constant value with increase in contact time because all the available sites were covered and no active site was further available for binding of dye molecules [12-16].

Effect of Initial pH

The initial pH of the dye solution is an important parameter which controls the adsorption

capacity. The results are shown in Fig. 5. The maximum %age removal of dye was obtained when the pH was 3.0 using *Raphanus sativus* peels, 7.0 using *Grewia asiatica* leaves and 2.0 in case of activated charcoal. The maximum %age removal of dye by using *Grewia asiatica* leaves was 96.35 %. In case of activated charcoal, the maximum %age removal of dye was 95.6 % and it was 87.26 % using *Raphanus sativus* peels. The results showed that *Grewia asiatica* leaves could easily remove dye in neutral conditions. The results indicated that the molecular form of Congo Red dye in solution medium changed markedly because its color changes from dark blue at pH 3.0 – 5.0 to red at pH 12.0. In addition, the red color is different from the original red in the pH range 10.0 –12.0. Color and its intensity change due to pH change are linked with the structural change which is occurring in the dye molecules. In the aqueous solution, the acid dye after dissolution, ionized as shown in this equation

$$D\text{-}SO_3Na \xrightarrow{H_2O} D\text{-}SO_3^- + Na^+ \qquad \text{(Eq.1)}$$

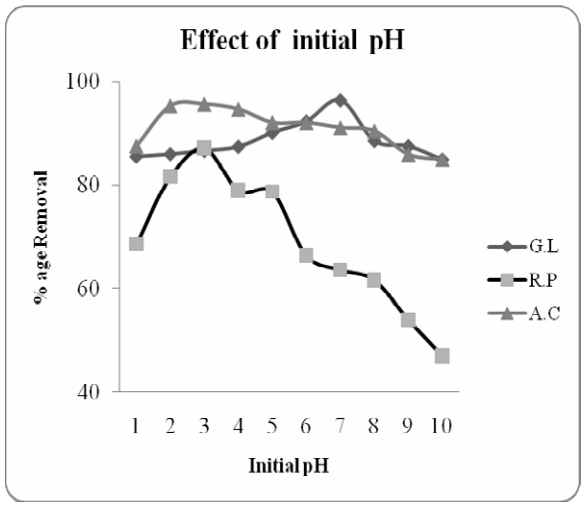

Fig.5: Effect of initial pH of dye solution using Raphanus sativus peels (R.P), Grewia asiatica leaves (G.L) and activated charcoal (A.C) on %age removal of Congo Red dye from water.

Fu and Viraraghavan [12] suggested that two primary amines ($-NH_2$) attached to the two naphthalene rings of the Congo Red molecule, can be protonated at the initial pH 6.0 and have stronger basicity which resulted in the attraction between the protonated amino groups of Congo Red molecule and negatively charged adsorbent surface, that results in more adsorption in acidic conditions.

Effect of Agitation Rate

The effect of variation in the agitation speed on the adsorption of Congo Red dye was studied. The results are shown in Fig. 6. Agitation is an important factor which influences the distribution of the solute in the bulk solution and formation of the external boundary film. The maximum %age removal of dye was obtained when the agitation rate was 100 rpm using *Raphanus sativus* peels and *Grewia asiatica* leaves, while 150 rpm in case of activated charcoal. By increasing the speed further, there was no further increase in adsorption rate. It was observed that adsorption yield increased with decrease in agitation rate. The maximum %age removal of dye by using *Grewia asiatica* leaves was 92.45 %. Activated charcoal had removed 93.53 % of dye and *Raphanus sativus* peels had adsorbed 66.96 %. All binding sites had been used at initial stage and no binding sites were further available for adsorption after some time. The degree of agitation reduces the boundary layer resistance and increases the mobility of the system. With agitation, the external mass transfer coefficient increases resulting in quicker adsorption of the dye molecules [12-18].

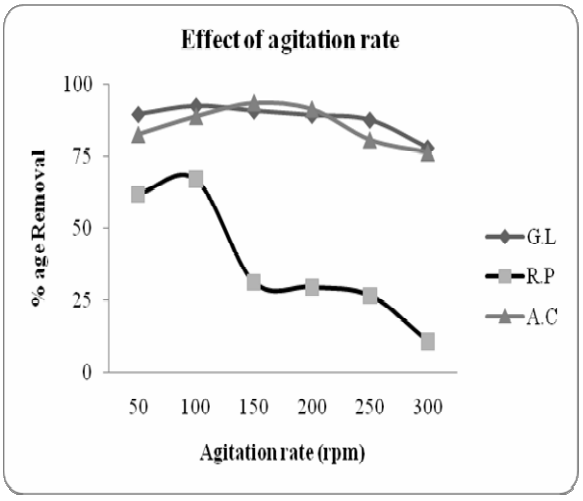

Fig.6: Effect of agitation rate on %age removal of Congo Red dye from water using Raphanus sativus peels (R.P), Grewia asiatica leaves (G.L) and activated charcoal (A.C).

Effect of Temperature

Temperature has a pronounced effect on the adsorption capacity of various adsorbents. The effect of this factor determined for temperatures ranging 10-80 ^oC. The results are shown in Fig. 7. The maximum adsorption values were obtained when the temperature was 20 $^\circ C$ using *Raphanus sativus* peels

(R.P) and activated charcoal as adsorbents and 30 ^{0}C using *Grewia asiatica* leaves. The maximum %age removal of dye by using *Grewia asiatica* leaves was 97.39 %. In case of coal, the maximum %age removal of dye was 85.91 % and it was 50.6 % using *Raphanus sativus* peels. The results showed that *Grewia asiatica* leaves could easily remove dye in normal conditions. Since adsorption is an exothermic process, it would be expected that an increase in temperature of the adsorbate–adsorbent system would result in decreased adsorption capacity [10-18].

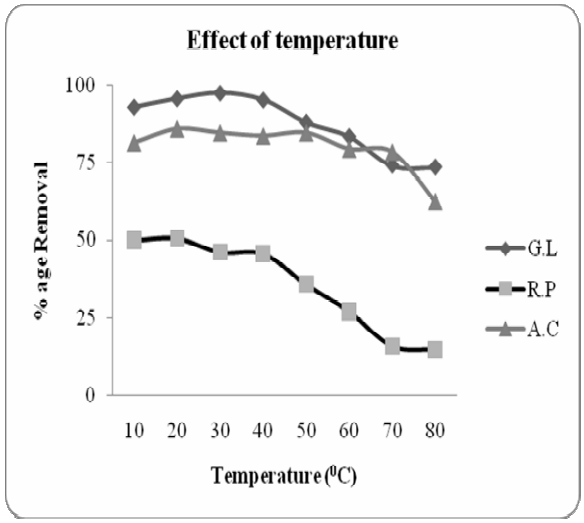

Fig.7: Effect of temperature on %age removal of Congo Red dye from water using Raphanus sativus peels (R.P), Grewia asiatica leaves (G.L) and activated charcoal (A.C).

Isothermal Studies

The Langmuir isotherms for Congo Red dye adsorption using *Raphanus sativus* peels (R.P), *Grewia asiatica* leaves (G.L) and activated charcoal (A.C) are shown in Fig. 8 and the corresponding parameters are given in Table-2. 'q_m' value was 0.069, 0.566 and 0.929 mg g^{-1} for Radish peels, *Grewia asiatica* leaves and activated charcoal respectively. The value of '*b*' for Congo Red dye was 0.743, 5.187 and 0.136 L g^{-1} for *Raphanus sativus* peels, *Grewia asiatica* leaves and activated charcoal correspondingly. The term '*b*' is an adsorption equilibrium constant related to apparent energy of adsorption. The correlation coefficient value (R^2) is approaching to one, which clearly suggested that Langmuir isotherm holds good to explain adsorption of Congo Red dye on *Raphanus sativus* peels, *Grewia asiatica* leaves and activated charcoal. The increasing values of '*b*' points out that increase in the adsorption will occur with increasing temperature but practically it decreases [12, 25, 26].

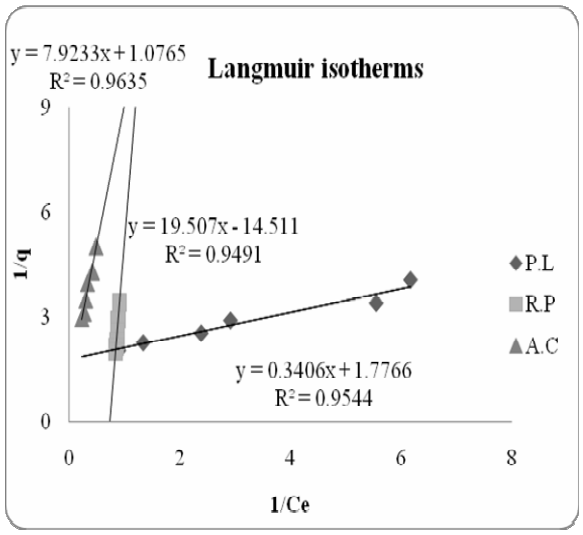

Fig.8: Langmuir isotherms for Congo Red dye adsorption from water using Raphanus sativus peels (R.P), Grewia asiatica leaves (G.L) and activated charcoal (A.C).

Table 2: Langmuir isotherm parameters for adsorption of Congo red dye.

Adsorbent	Langmuir Isotherm Parameters		
	R^2	q_m (mg g^{-1})	b (L g^{-1})
R.P	0.9491	0.069	0.743
G.L	0.954	0.566	5.187
A.C	0.9635	0.929	0.136

Where, R.P = Raphanus sativus Peels, G.L = Grewia asiatica leaves and A.C = Activated Charcoal.

Effect of Chemical Modification of Adsorbents

The effect of chemical modification of adsorbent is shown in Fig. 9. It is clear from the graph that maximum %age removal of dye is observed when urea modified *Grewia asiatica* leaves were used. Generally the colored and resinous components of adsorbents were extracted out in organic solvents which enhanced their adsorption capacity as compared to non-modified adsorbents. Non-polar solvents like carbon tetrachloride, benzene or chloroform had not greatly changed the adsorption capacity of these adsorbents because they did not alter the adsorption sites.

Experimental

Materials and Methods

Congo Red dye (Merck, C.I. = 22120, chemical formula = $C_{32}H_{22}N_6Na_2O_6S_2$, FW= 696.7 g/mol, λmax = 500 nm), HCl (Merk, 11.6 M), NaOH (Merck, Mol.wt = 40 g/mol). Electric Balance ER-120A (AND), Electric grinder (Ken Wood), pH meter (HANNA pH 211), Perkin-Elmer-RX-FT-IR

spectrophotometer and UV-Vis Double Beam spectrophotometer (UVD-3500, Labomed) were used. Double distilled water was consumed for all types of solution preparations, rinsing and dilutions where ever required. 1.0 g of Congo Red dye was dissolved in 1000 mL measuring flask in water for making stock solution. Standard solutions of dye were prepared by appropriate dilution of this solution.

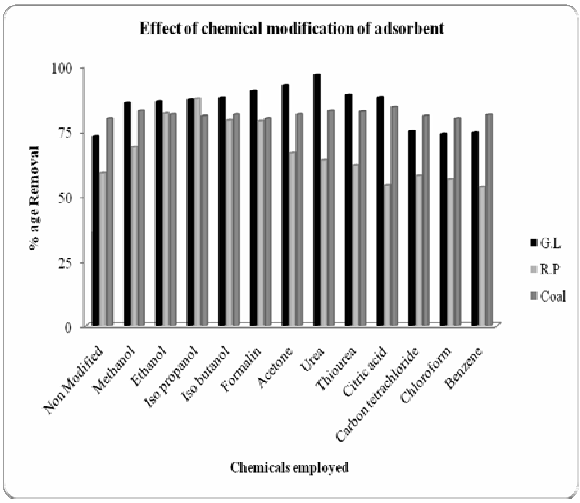

Fig.9: Effect of chemical modification on adsorption efficiency of Raphanus sativus peels (R.P), Grewia asiatica leaves (G.L) and activated charcoal (A.C) on %age removal of Congo Red dye from water.

Preparation of Adsorbents

The Radish (*Raphanus sativus var. longipinnatus*) was purchased from local market of Lahore, Pakistan. Radish were washed and peeled off. The *Grewia asiatica* (Phalsa) leaves were collected from the gardens of University of Punjab, New Campus, Lahore, Pakistan. *Raphanus sativus* peels and *Grewia asiatica* leaves were air dried in the presence of sunlight for 3-4 days to remove moisture completely, followed by oven drying at 60 $^{\circ}$C for 3-4 hours, in order to get constant weight. After that, the materials were ground. Charcoal sample is obtained from local market of Lahore and was further purified and activated by washing five times with distilled water and heating at 450 ^{0}C for one hour. Then it was ground and stored in a vacuum desiccator. Their FT-IR spectra were recorded and resulting peaks are summarized in Table-1.

Adsorption Experiments

All the experiments were carried out at 25 ± 1 °C. A known amount of different adsorbents was added to sample solution of dye separately and kept for some time to attain adsorption equilibrium. 0.1 N HCl and 0.1 N NaOH were used for adjusting pH of the solution according to the requirement. After required time interval, dye solutions were filtered and remaining concentration of dye was determined in the filtrate, using UV-Vis double beam spectrophotometer working at 500 nm (λ_{max} of Congo Red dye).

Various factors which affect adsorption process were studied by varying particle size of adsorbent (20-30 to 80-100 microns mesh size), adsorbent amount (0.5-2.5 g), contact time (10-60 min), initial pH of the solution (1-10), agitation speed (50-300 rpm) and temperature (10-80 °C). The solution volume (V) was kept constant (50 mL). The %age removal of dye at any instant of time was determined by the following equation:

$$\%\,\text{age Removal of Dye} = \frac{C_o - C_e}{C_o} \times 100 \qquad \text{(Eq.2)}$$

where C_o and C_e are the concentrations of dye before and after biosorption respectively. Each experiment was repeated three times for increasing accuracy of the data and average values were used for calculations.

Study of Adsorption Isotherm

50 mL of six solutions with concentrations 10, 15, 20, 25, 30 and 35 ppm were prepared by proper dilution of stock solution of the dye. The optimized conditions of all parameters like adsorbent particle size, initial pH, adsorbent dose, agitation speed, contact time and temperature were employed according to the sample of adsorbent used for studying adsorption isotherm. At the end, solutions were filtered off and filtrates were analyzed for remaining dye concentration in order to obtain isotherm plot.

Data Evaluation

Adsorption properties and equilibrium parameters are described by using adsorption isotherms. In order to optimize the design of adsorption system to remove dye from solutions, it is essential to find the most appropriate correlation for equilibrium curve. Mostly Langmuir isotherm is applied for analyzing experimental biosorption equilibrium parameters.

The basic assumption of Langmuir isotherm is that there is a fixed number of binding sites which are homogeneously distributed over the adsorbent surface. These binding sites have the same affinity

for adsorption of a single molecular layer and there is no interaction between adsorbed molecules. It was plotted by using its standard straight-line equation (Eq. 3):

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \qquad \text{(Eq. 3)}$$

The value of q is calculated by using the formula:

$$q = \frac{(C_o - C_e)V}{m} \qquad \text{(Eq. 4)}$$

where the term 'q' (mg g^{-1}) is the amount of dye adsorbed, 'C_e'(ppm) is the remaining concentration of dye after adsorption, 'q_m' (mg g^{-1}) and b (L g^{-1}) are Langmuir isotherm parameters which were calculated from the slope and intercept values of the graph between '1/q' versus '1/ C_e'. Whereas 'V' (L) is the volume of dye solution, 'm' (g) is the mass of adsorbent used [25, 26]

Chemical Modification of Adsorbents

All the adsorbents of 50 microns mesh size were modified with different organic solvents and chelating agents. Organic solvents like methanol, ethanol, iso-propanol, iso-butanol, formalin and acetone, carbon tetrachloride, benzene and 10 % aqueous solution of various chelating agents like urea, thiourea, citric acid and tartaric acid were used for modification of adsorbents. Equal amount of adsorbents were treated with equal volume of all these solution separately in the beakers and after covering with aluminum foils, they were kept for three hours. After filtering and drying, 0.5 g of all the modified biosorbents were treated with 20 mL of 10 ppm dye solution separately. After agitating at 100 rpm for 15 minutes, all the solutions were filtered and the remaining dye concentration was determined. Then %age removal of dye was calculated and plotted in Fig. 9.[28-30].

Conclusion

From this study, it was observed that *Grewia asiatica* leaves powder is an effective adsorbent for the removal of Congo Red dye from aqueous media. Its chemical modification with urea increases its adsorption efficiency, while *Raphanus sativus* peels are comparatively less effective in this regard. *Grewia asiatica* leaves powder efficiency of adsorption is comparable with charcoal. So, it can be used on larger scale for the treatment of wastewater containing Congo Red dye.

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