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Mechanistic and Characterization Studies for Sorptive Elimination of Emerald Green Dye from Water By *Arachis hypogeal* Shells and *Citrullus lanatus* Peels

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Emerald green dye adsorption by *Arachis hypogeal* shells and *Citrullus lanatus* peels has been investigated in this study. Characterization of adsorbents by measuring pH, bulk density, pH_{pzc}, porosity, iodine number, moisture contents, ash contents, elemental contents, carboxylic (acidic functions), phenolic, lactonic and basic sites were conducted.The adsorption process was done in a batch process by varying contact time intervals, adsorbent doses, different initial pH, agitation speed and temperature. The suitability of the data was confirmed by determining isothermal parameters, which showed that sorption capacity of *Citrullus lanatus* peels for Emerald green dye is 2.099 mg g^{-1} with ΔG^0 -2.785 KJ mol^{-1} and it is better adsorbent as compared to *Arachis hypogeal* shells, which adsorbs only 1.989 mg g^{-1} of dye with ΔG^0 -1.432 KJ mol^{-1}. Both of them can be used on larger scale water treatment for removing Emerald green dye.

Keywords: *Citrullus lanatus* peels, *Arachis hypogeal* shells, Adsorption, Emerald green dye, Adsorption isotherms.

INTRODUCTION

Dyes present in wastewater is a serious environmental issue because it is highly toxic and presents serious environmental problems[1]. About 10000 different dyes and pigments are utilized by the textile industry. The annual synthetic dye production precedes over 7×10^5 metric tons globally[2]. Dyes which are used in dye stuffs and textile industries, 10-15 % of all is directly released as without utilization in the effluents and are major cause of environmental health because they are exposed into water streams[3]. Dyes are ionic aromatic organic compound[4]. In plastic, textile, food, cosmetic and paper industries they are used as colouring agents[5,6]. In literature, 40,000 colourants are listed that consists of 7,000 different chemical structures[7]. They mainly cause problems due to non-biodegradable nature and unpleasant colour producing tendency[8]. It is reported that textiles industries consume more than 60 % of the dyes production worldwide[9]. For some microorganisms dyes are toxic and may cause inhibition of their catalytic capabilities or direct destruction[10]. Industries use photocatalysis[11], biological treatment[12], coagulation-flocculation[13], hyper-filtration, oxidation and adsorption for removal of dyes[14]. Adsorption is very effective technique for the wastewater treatment, due to simplicity and low cost material usage[15].

Emerald green (E.G) is triarylmethane, cationic dye (Fig. 1). It is known as 4,4-*bis*diethylaminotriphenyl methylsulfate[16]. It is yellow-green to green, odorless and powdered dye used as veterinary medicine, dermatological agent and biological stain. It is used in poultry feed as an additive, in order to inhibit the reproduction of germs[17]. It is also used for colouring purposes: dying wool, silk, leather and paper industries[18]. Consumption of this dye is 0.8-1.0 Kg per ton of paper formed. It is used to make green inks and as an indicator[19]. In human's gastrointestinal tract, it causes irritation whose symptoms include vomiting, nausea and diarrhea[20]. It is also used as a selective bacteriostatic agent and as a topical antiseptic[21] in culture media. In humans and animals, it causes eye burns that may lead to the permanent injury to eyes[22]. Due to decomposition on heating, it may form hazardous products like sulfur dioxides and nitrogen oxides[19].

In the present research work removal of hazardous cationic, triphenyl dye containing nitrogen *i.e.* Emerald green dye from aqueous medium is carried out by using peanut (*Arachis hypogea*) shells and water melon (*Citrullus lanatus*) peels as adsorbent. Peanut (*Arachis hypogea*) is an oil producing plant found in Asian countries extensively. So it is agricultural by-product which is inexpensive and abundant[23]. Most of the peanut shells were either abandoned or slugged for fuel as an agricultural waste which results in waste of natural resources. Recently, for treatment of wastewater interest in developing peanut shells have been reported by several studies[24]. On the other hand, water melon (*Citrullus lanatus*) is a vine-like plant of Cucurbitaceae family. This is a flowering plant that produces a special fruit which is known as a pepo[25].

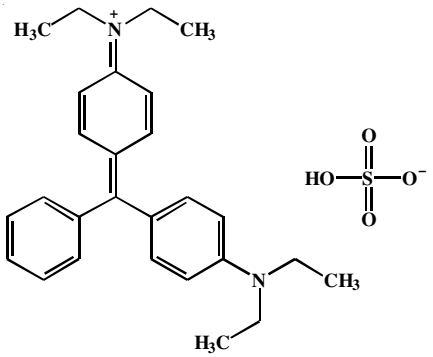

Fig. 1. Structure of Emerald green dye

Water melon peels is a common by-product of agriculture. It contains high level of citrulline, which has potential vasodilation and antioxidant role in nitric oxide system of humans[26].The purpose of this study was to characterize the peanut shells and water melon peels and to find the optimal conditions for better dye removal.

EXPERIMENTAL

Emerald green dye (synonyms: malachite green-G, brilliant green, diamond green-G and λ_{max}: 625 nm), hydrochloric acid (37 %, 11.6 M), sodium hydroxide (mol. wt. 40 g/mol), sodium chloride (mol. wt. 58.5 g/mol), sodium bicarbonate (mol. wt. 84 g/mol), calcium carbonate (mol. wt. 100 g/mol, nickel sulphate hexahydrate (mol. wt. 263 g/mol), copper sulphate pentahydrate (mol. wt. 249.68 g/mol) were obtained from Friends laboratory chemicals. Cadmium chloride monohydrate (mol. wt. 201.32 g/mol), zinc chloride (mol. wt. 136.28 g/mol), potassium chromate (mol. wt. 194.20 g/mol) were obtained from Merck (Germany). Iodine crystals (mol. wt. 253.81 g/mol, 99.8 %) from Acros Organic and all others like potassium iodide (mol. wt. 166 g/mol), sodium carbonate (mol. wt. 58.5 g/mol), phenolphthalein, methyl orange, magnesim chloride hexahydrate (mol. wt. 95 g/mol), manganese chloride monohydrate (mol. wt. 143.86 g/mol), lead nitrate (mol. wt. 331.21 g/mol) were purchased from Riedel-de-Haen, Friends laboratory chemicals.

Electric grinder, weighing balance (VELP Scientifica 230 V, 50 Hz), electrical furnace (ranging from 30-1200 °C) Naberthem B170, pH paper (Merck), UV/visible Spectrophotometer (wavelength range 190-1100 nm), APEL PD-303 UV, orbital shaker (model OSM-747) Digiteck instruments.

Preparation of adsorbents: The peanut shells and water melon peels used here were collected from the native market of Lahore (Pakistan). This collected material was washed thoroughly in order to remove dust and soil particles. Then it was air dried followed by oven drying at 70 °C. Primary grinding of dried material was performed in pin mill, fitted with 50 mesh screen.

Characterization of adsorbents: Characterization of both the adsorbents was done by determining the pH, pH_{pzc}, bulk density, porosity and iodine number, moisture contents, ash contents, volatile organic contents, carboxylic (acidic functions), phenolic, lactonic and basic sites, using Ekpete and Horsfall methodology[27-29] and results were presented in Figs. 2 and 3 and Table-1.

TABLE-1
PHYSICO-CHEMICAL ANALYSIS OF ADSORBENTS

Property			*Arachis hypogeal* shells	*Citrullus lanatus* Peels
pH			6	7
Particle density (g/cm^3)			0.231	0.5
Bulk density P_{wet} (g/cm^3)			0.952	0.95
Porosity (%)			0.152	0.143
Moisture (%)			6.5	8
Ash (%)			4.6	2.2
Volatile matter (%)			20	28
Iodine number (mg/g)			4.23	2.108
Carboxylic (acidic functions)			1.98	1.99
Phenolic			0.003	0.004
Lactonic			0.002	0.006
Basic sites			1.984	1.98
pH_{pzc}			4	6
pH			6	7
Elemental contents	Macro-nutrients	K(I)	8	14.807
		Na(I)	4	21.1
		Mg(II)	0.375	0.342
		Ca(II)	0.776	0.3
		Fe(II)	0.088	0.038
	Micro nutrients	Mn(II)	0	0
		Ni(II)	0	0
		Cu(II)	0	0
		Zn(II)	0	0

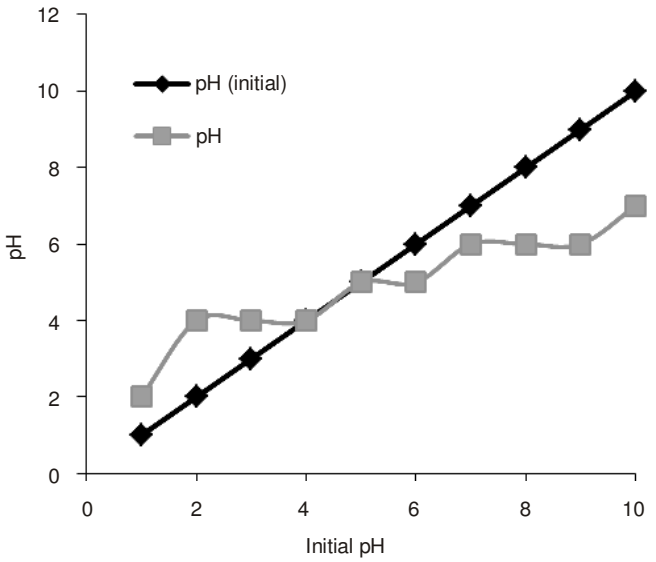

Fig. 2. Determination of point of zero charge (pH_{pzc}) for *Arachis hypogeal* shells

Synthetic wastewater solution of Emerald green dye: In order to make 1000 ppm stock solution of dye, its 1 g of the dye was dissolved per liter. Standard solutions (5-25 ppm) of dye were prepared from the stock solution by dilution.

Batch adsorption experiments: The batch adsorption experiments were carried out separately using both adsorbents, in order to optimize adsorption parameters for removing Emerald green dye, like: contact time, pH of dye solution, adsorbent dose, temperature and agitation speed, followed by isothermal studies for determining mechanism of sorption and thermodynamic feasibility of this process on industrial scale. Same procedure is followed as described earlier[30]. The percentage adsorption of dye is calculated by eqn. 1:

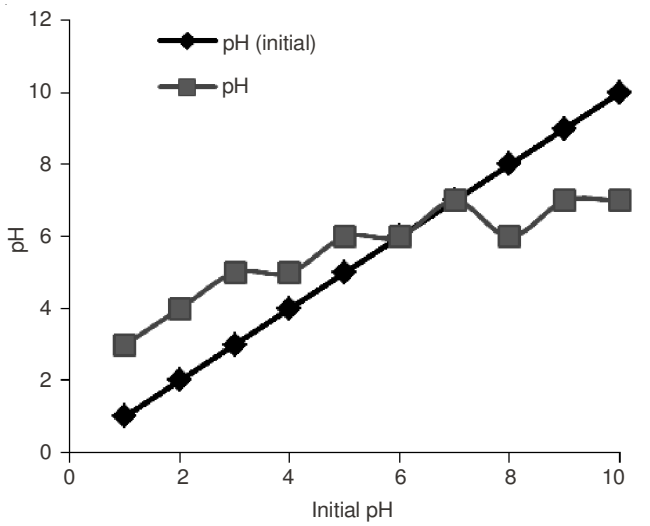

Fig. 3. Determination of point of zero charge (pH_{pzc}) for *Citrullus lanatus* peels

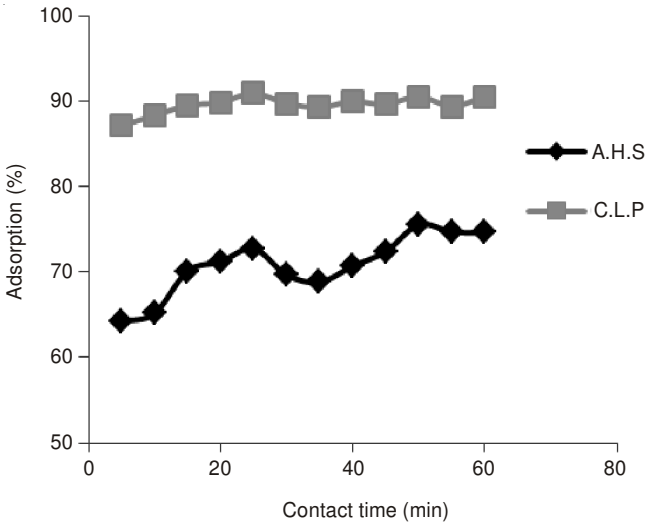

Fig. 4. Comparative graph showing effect of Contact Time on Emerald green dye adsorption using *Arachis hypogeal* shells (A.H.S) and *Citrullus lanatus* peels (C.L.P)

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

Initial concentration 'C_0' is 25 ppm, while remaining concentration 'C_e' is determined spectrophotometrically using standard solutions of dye at 625 nm λ_{max}. In order to reduce the chances of errors,experiment were conducted in duplicate for recording average values to make graphs.

RESULTS AND DISCUSSION

Characterization of adsorbents: Table-1 is showing that *Arachis hypogeal* shells are basic in nature, having more bulk density and porosity as compared to *Citrullus lanatus* peels. Unsaturated functional groups in adsorbents enhance their chelating nature, in turns increasing sorption capacity. It is found that *Arachis hypogeal* shells contain more unsaturated compounds, as indicated from its iodine value. *Citrullus lanatus* peels contain more acidic functional groups as compared to *Arachis hypogeal* shells, as indicated from higher values of acidic contents like: carboxylic, phenolic and lactonic sites. Figs. 2 and 3 are showing pH_{pzc} value of *Arachis hypogeal* shells and *Citrullus lanatus* peels. It is indicating that they can work better for basic type of pollutants, instead of acidic type[27-29].

Effect of contact time: It was studied from 5 to 60 minutes interval with variation of 5 min. each, between adsorbents and dye solution, using *Arachis hypogeal* shells and *Citrullus lanatus* peels separately. The results are shown in Fig. 4.

In case of *Arachis hypogeal* shells the maximum percentage adsorption occurred within 50 minutes and it was 75.54 %. In case of *Citrullus lanatus* peels, maximum percentage removal occurred within 25 min. and it was 90.90 %.The results showed that the *Citrullus lanatus* peels can remove more quantity of Emerald green dye from water as compared to *Arachis hypogeal* shells in comparatively less time. The rate of adsorption first increase with increase of contact time and then decreased to constant value, because there are no active sites present for attaching dye to adsorbent surface[22,25].

Effect of adsorbent dosage: It was studied in range of 0.3 to 3 g with variation of 0.3 g each, using *Arachis hypogeal* shells and *Citrullus lanatus* peels. The results are presented in Fig. 5. In case of *Arachis hypogeal* shells maximum percentage dye removal from aqueous solution was occurred when 2.4 g of adsorbent dose was used and it was 76.86 %. In case of *Citrullus lanatus* peels the maximum percentage dye removal was 84.06 % when 1.8 g of adsorbent dose was used. There is an increase in the percentage dye sorption with increase of adsorbent dosage because more adsorption sites were available[9, 15-17].

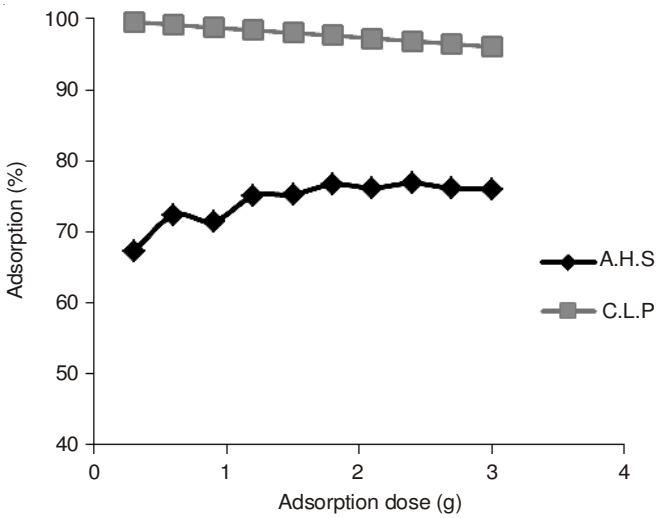

Fig. 5. Comparative graph showing effect of adsorbent dose on Emerald green dye adsorption using *Arachis hypogeal* shells (A.H.S) and *Citrullus lanatus* peels (C.L.P)

Effect of pH: The effect of initial pH on biodegradation of Emerald green dye was studied ranging from 1 to 10. Initial pH of the dye solution was controlled by using 0.01 M NaOH/ 0.01 M HCl solutions. The results are shown is Fig. 6. In case of *Arachis hypogeal* shells the maximum percentage adsorption occurred at a pH of 4 and it was 75.46 %. This pH value resembles with its pH_{pzc} value. But in case of *Citrullus lanatus*

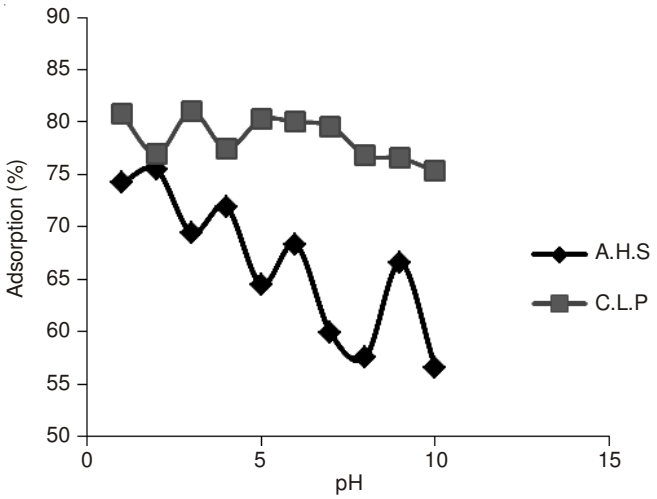

Fig. 6. Comparative graph showing effect of pH on Emerald green dye adsorption using *Arachis hypogeal* shells (A.H.S) and *Citrullus lanatus* peels (C.L.P)

peels, maximum percentage removal occurred at a pH of 3. It was 81.01 %. The pH value has a pronounced effect on the stability of Emerald green molecule structure[7,17,22]. It was observed that solution of Emerald green dye is stable in acidic media and become precipitated in basic media. Therefore, pH 4 for *Arachis hypogeal* shells and 3 for *Citrullus lanatus* peels was selected for further experimental work.

Temperature effect: Adsorption effect of temperature ranging from 20-70 °C was studied with variation of 10 °C each was studied and graphically presented in Fig. 7. At 50 °C, maximum percentage adsorption was observed, *i.e.* 85.34 % and 85.99 % using *Arachis hypogeal* shells and *Citrullus lanatus* peels respectively. Adsorption is an exothermic process. In addition to that, biosorbents are swelled out, because of the presence of various biopolymers in their structures, exposing more adsorption sites at higher temperatures[6,7,22].

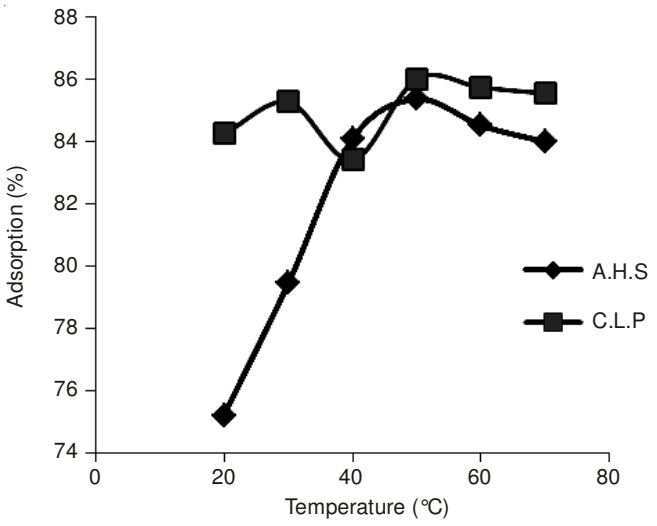

Fig. 7 Comparative graph showing effect of temperature on Emerald green dye adsorption using *Arachis hypogeal* shells (A.H.S) and *Citrullus lanatus* peels (C.L.P)

Effect of agitation speed: It was studied from 25 rpm to 200 rpm with variation of 25 rpm each using *Arachis hypogeal* shells and *Citrullus lanatus* peels. The results are given in Fig. 8. Using *Arachis hypogeal* shells, maximum percentage elimination of dye was 84.05 % when the agitation speed was 150 rpm and using *Citrullus lanatus* peels, maximum percentage sorption was 92.44 % at 100 rpm. There is no improvement in adsorption rate with further increase of agitation speed, because of unavailability of further binding sites as all the binding sites are utilized in this process[7-9].

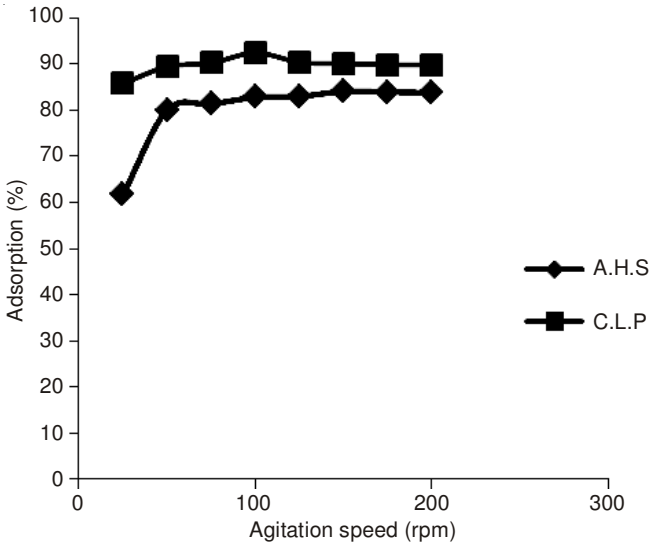

Fig. 8. Comparative graph showing effect of agitation speed on Emerald green dye adsorption using *Arachis hypogeal* shells (A.H.S) and *Citrullus lanatus* peels (C.L.P)

Adsorption isotherms: All factors optimized conditions were employed for studying adsorption isotherms, in order to find mechanism of sorption.

Langmuir model:

It can be represented by the following equation;

$$\frac{1}{q} = \frac{1}{q_m \times b \times C_e} + \frac{1}{q_m} \quad (2)$$

In Langmuir isotherm theory it is assumed that the adsorbed layer in one molecule in thickness (monolayer adsorption). Here 'q' is calculated through this formula:

$$q = \frac{(C_0 - C_e)V}{m} \quad (3)$$

Thermodynamic parameter 'ΔG°' was calculated from eqn. 4:

$$\Delta G^\circ = -RT \ln K \quad (4)$$

where, q_m = monolayer (maximum) capacity of adsorption in mg g^{-1}.

b = constant related to the adsorption energy in L g^{-1}.

ΔG° is in KJ mol^{-1}. Negative ΔG° values confirmed the spontaneous nature of adsorption.

For adsorption of Emerald green dye, the Langmuir isotherms using *Arachis hypogeal* shells and *Citrullus lanatus* peels are shown in Fig. 9 and related parameters are shown in Table-2.

For *Arachis hypogeal* shells, maximum sorption capacity 'q_m' was 1.989 mg g^{-1} and it was 2.099 mg g^{-1} in case of *Citrullus lanatus* peels. Whereas, the value of 'b' was 0.561 L g^{-1} and

TABLE-2
LANGMUIR ISOTHERMAL PARAMETERS FOR ADSORPTION OF EMERALD GREEN DYE

Adsorbent	Slope	Intercept	R^2	q_m (mg g^{-1})	b (L mg^{-1})	ΔG^0 (KJ mol^{-1})
Arachis hypogeal shells	0.896	0.503	0.944	1.989	0.561	-1.432
Citrullus lanatus peels	1.467	0.476	0.954	2.099	0.325	-2.785

TABLE-3
FREUNDLICH ISOTHERMAL PARAMETERS FOR ADSORPTION OF EMERALD GREEN DYE

Adsorbent	Slope	Intercept	R^2	K_F ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1})	n
Arachis hypogeal shells	1.521	0.267	0.994	1.849	0.658
Citrullus lanatus peels	1.435	0.447	0.994	2.798	0.696

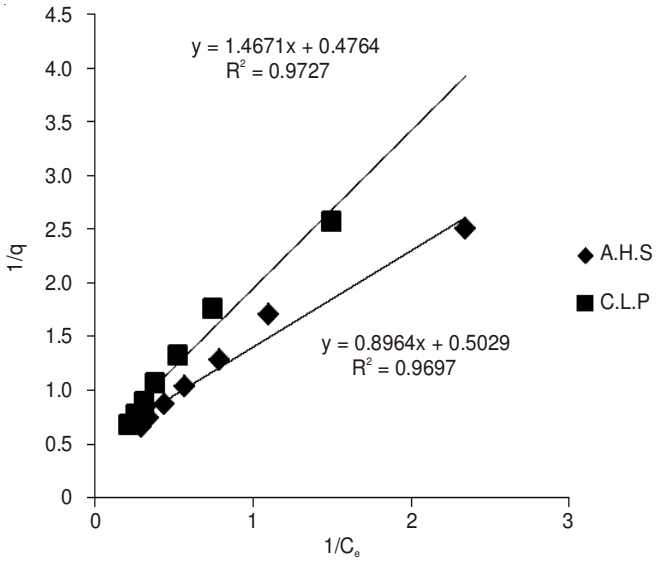

Fig. 9. Langmuir isotherms for Emerald green dye adsorption from water using *Arachis hypogeal* shells (A.H.S) and *Citrullus lanatus* peels (C.L.P)

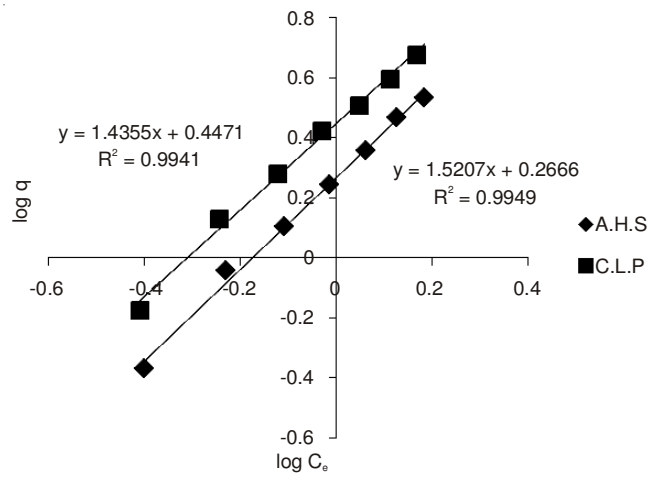

Fig.10. Freundlich isotherms for Emerald Green dye adsorption from water using *Arachis hypogeal* shells (A.H.S) and *Citrullus lanatus* peels (C.L.P).

0.325 L $g^{-1}$for *Arachis hypogeal* shells and *Citrullus lanatus* peels respectively. The correlation coefficient (R^2) is near to one, which suggests the Langmuir isotherm holds very good in order to explain the adsorptive removal of Emerald green dye on *Arachis hypogeal* shells and *Citrullus lanatus* peels[7,8,15,24].

Freundlich model: The isotherm constants studied using both adsorbents and correlation coefficients (R^2) are shown in Fig. 10, which was drawn using eqn. 5. Here 'K_F' and 'n' are Freundlich isotherm constants. 'K_F' value was 1.84 and 2.79 $mg^{1-(1/n)}$ $L^{1/n}$ g^{-1} for *Arachis hypogeal* shells and *Citrullus lanatus* peels respectively. It shows that physiosorption is equally important for sorptive removal of dye, along with chemisorption. For Emerald green dye the value of 'n' was 0.658 using *Arachis hypogeal* shells and 0.696 L mg^{-1} for *Citrullus lanatus* peels. It means that *Citrullus lanatus* peels contain more heterogeneous surface. It is also supported by characterization studies given in Table-3.

$$\log q = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

Conclusion

From these results, it is obvious that *Citrullus lanatus* peels is better adsorbent for sorptive elimination of Emerald green dye from water as compared to the *Arachis hypogeal* shells. Characterization studies reveal that *Citrullus lanatus* peels contain more acidic sites for binding, but less porosity. This is helpful for chemisorptive removal of Emerald green dye, whereas due to more porosity and less moisture contents, *Arachis hypogeal* shells remove Emerald green dye by physiosorption mode. It is also confirmed by isothermal studies. The negative $\Delta G°$ values showed that the adsorption process was spontaneous.

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