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Removal of Alizarin Yellow and Murexide Dyes from Water Using Formalin Treated *Pisum sativum* Peels

RABIA REHMAN*, TARIQ MAHMUD and AYESHA ARSHAD

Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan

*Corresponding author: Fax: +92 42 99230998; Tel: +92 42 99230463, Ext: 870; E-mail: grinorganic@yahoo.com

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Adsorption process is eco-friendly which is used for the removal of dyes. In this research work, formalin treated *Pisum sativum* peels were used for the removal of Murexide and Alizarin yellow from water. Various parameters like adsorbent dose, pH, temperature, agitation speed and contact time were investigated. Three isotherms Freundlich, Langmuir and Temkin were used to elucidate the observed adsorption phenomenon. Freundlich adsorption isotherm was best fitted with maximum removal of 2.47 and 11.04 mg/g of Alizarin yellow and Murexide, respectively. From this research work, it is concluded that peels of *Pisum sativum* were proved efficient and effective adsorbents for the removal of Alizarin yellow and Murexide.

Keywords: *Pisum sativum* peels, Murexide, Alizarin yellow, Adsorption.

INTRODUCTION

Water is an indispensable requirement of life but it is polluted by various types of pollutants when discharged directly or indirectly into water[1]. Dyes are the main constituents of effluents. Recently, there is an increasing trend of dyes removal from water due to their non-biodegradation and poisonous nature. In spite of various techniques are available for the treatment of waste water, there is no solo process which is sufficient for the treatment of these effluents. Adsorption phenomenon is relatively popular and accepted due to presence of large range of biomasses and this technique proved it self as an efficient, effective and appealing process for removal of non-biodegradable pollutants[2-5] like dyes[6]. A lot of research have been done for the removal of dyes by using various biosorbents such as rice husk[7], coffee husks[8], mango seeds[9] and many others. Large amount of agricultural production are grow all over the world and waste is rejected. So, scientists are trying to use this agricultural waste for useful purposes. These wastes are lingo-cellulosic material. If these agricultural wastes are dispose of into the environment may pollute our land, air and water and hence damage our ecosystem. So in order to overcome this type of pollution, many processes have been introduced. One of them is to use this agricultural waste as adsorbent for the removal of industrial effluents especially for dyes. These agricultural wastes have better adsorptive properties for the removal of dyes than other adsorbents. These adsorbents are easily available, less expensive and renewable and are used without or with minimum processing such as washing, drying and grinding.

In the present research work, *Pisum sativum* (pea) peels are used as an adsorbent for the removal of Alizarin yellow and Murexide. *Pisum sativum* is botanically fruit but also considered as vegetable. It is grown for its seeds, having little or no fats so having no cholesterol[10]. Alizarin yellow is a mordant azo dye (Fig. 1). It is formed by diazo coupling reaction. It is rust coloured solid in pure form. Its molecular formula is $C_{13}H_8N_3O_5Na$, having molecular mass 309.21 g mol^{-1} and λ_{max} is 370 nm. Alizarin yellow habitually exists as sodium salt and is soluble in cold water. Its colour changes from light yellow in acidic pH to orange yellow in basic pH[11]. It is used to colour nylon, wool, leather, furs and anodized aluminum[12]. If it is inhaled then may cause gastro intestinal tract discomfort and may also produce nausea and vomiting. If this dye is in direct contact with eyes may cause irritation and redness and in some cases tearing, slight abrasive damage in eyes may occur.

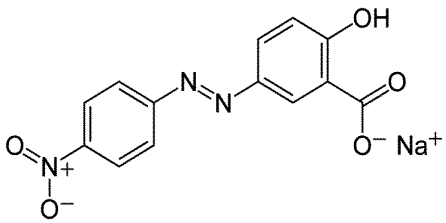

Fig. 1. Alizarin yellow

Murexide with a chemical formula of $NH_4C_8H_4N_5O_6$. The other name of Murexide is ammonium purpurate. Its molar

mass is 284.19 g/mol and λ_{max} is 525 nm. The structural formula is given in Fig. 2. It is a reddish purple powder. Its colour changes from yellow in strong acidic pH to reddish purple in weak pH and in alkaline solutions it shows blue purple colour[13]. It is useful as purple dye for wool. It is also used as an indicator in many complexometric titrations. Murexide is also used as a colourimetric reagent for the measurement of copper, zinc, nickel, cadmium, strontium and calcium[14-17]. Due to its various uses, its significant amount goes in waste water and then ultimately into ocean and pollute aquatic bodies. Murexide may cause conjunctiva redness or tearing, if direct contact with eyes occurs. It may also produce skin irritation in certain individuals. It is injurious if inhaled.

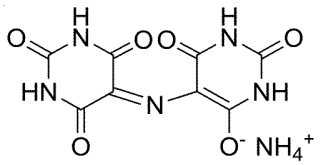

Fig. 2. Murexide

EXPERIMENTAL

Murexide (Fluka), Alizarin yellow (Fluka), NaOH (Merck), HCl (Merck), Na_2CO_3 and $NaHCO_3$ (Friend's Chemical Laboratory), KBr. Orbital shaker (time control), UV/visible spectrophotometer (Labomed, 3500), Atomic absorption spectrophotometer (Perkin Elmer Analyst 100), Electric Furnace, FT-IR (Prestige-21 SHIMADZU DRS-80000, No of scans-50).

Adsorbent preparation: Peels of *Pisum sativum* were collected from local market. They were washed, dried, grinded and sieve trough 50 size mesh (ASTM). Formalin solution was prepared in water with 1:1 ratio. 100 g of of *Pisum sativum* peels powder was soaked in 1 L of this formalin solution for 12 h in different beakers. Then it was filtered and washed with distilled water until filtrate became almost colourless. Then again these adsorbents were air dried and then dried in oven at 70 °C for 0.5 min. After drying, these adsorbents were homogenized in mortar and pestle then stored in bottles.

Determination of moisture content: Thermal drying process was used to determine the moisture content of the samples. 1 g of the dried adsorbents (*Pisum sativum*) were weighed in triplicates separately and placed in washed and dried crucibles in oven for 5 h and then weighed and determined the moisture content by using this eqn. 1.

$$\text{Moisture (\%)} = \frac{\text{Loss in weight on drying (g)}}{\text{Initial weight (g)}} \times 100 \quad (1)$$

Determination of pH: For the determination of pH, 1 g of each adsorbent of *Pisum sativum* (untreated and formalin treated) was taken in a beaker with 100 mL of distilled water and stirred for 1 h. When samples were stabilized then pH meter was used to determine the pH. Samples were run in triplicates.

Determination of oxygen containing functional groups: Oxygen containing functional groups were determined by Boehm titration method. 1 g of each adsorbent was taken in contact with 15 mL solution of $NaHCO_3$ (0.1 M), Na_2CO_3 (0.05 M) and NaOH (0.1 M) for acidic groups and HCl (0.1 M) for basic sites at room temperature for 2 days. Then back titrated with 0.1 M HCl for acidic sites and 0.1 M NaOH for basic sites by using phenolphthalein and methyl orange as indicators. The acidic sites were calculated by considering that NaOH neutralizes carboxylic, phenolic and lactonic groups, Na_2CO_3 neutralizes lactonic and carboxylic groups and $NaHCO_3$ neutralizes carboxylic groups. HCl determines the basic sites by neutralizing them.

Determination of metal ions: For the determination metal ions in the adsorbents, 1 g of biomass was taken in the washed crucibles and digested them with 0.2 mL HNO_3. Then these samples were kept in Muffle furnace at 550 °C until converted into white ash. This white ash was dissolved in distilled water and diluted upto 100 mL after filtering undissolved matter. Then filtrate was used for the determination of presence of macro-nutrient metal ions (K^+, Na^+, Mg^{2+}, Fe^{2+}), micro (Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and toxic metals (Zn^{2+}, Cr^{6+}, Pb^{2+}, Cd^{2+}) by using flame photometer and Perkin Elmer AAS.

Determination of functional groups: For the determination of various functional groups present in the adsorbents FT-IR spectra were recorded and given in Figs. 3 and 4. For this purpose, 0.3 g of the adsorbent was grinding with 0.7 g of the powdered KBr in smooth way by using mortar and pastel. Then this solid mixture was compressed to form a pellet for analysis.

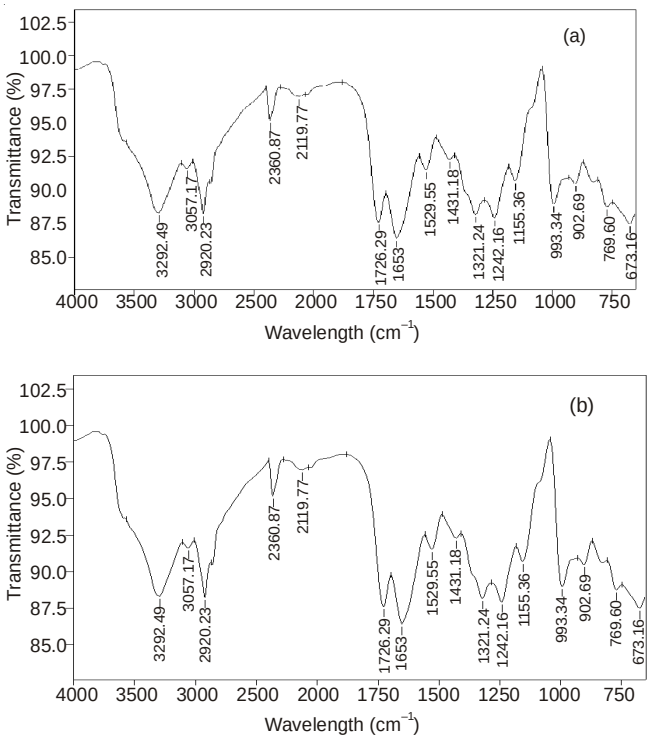

Fig. 3. FT-IR spectra of *Pisum sativum* peels (a) untreated (b) formalin treated

Adsorption studies: The adsorption studies were carried out in a series of experiments to study the effect of various parameters. The percentage of dye adsorption was determined at any instant of time by the following eqn. 2:

$$\text{Adsorption (\%)} = (C_o\text{-}C_e/C_o) \times 100 \quad (2)$$

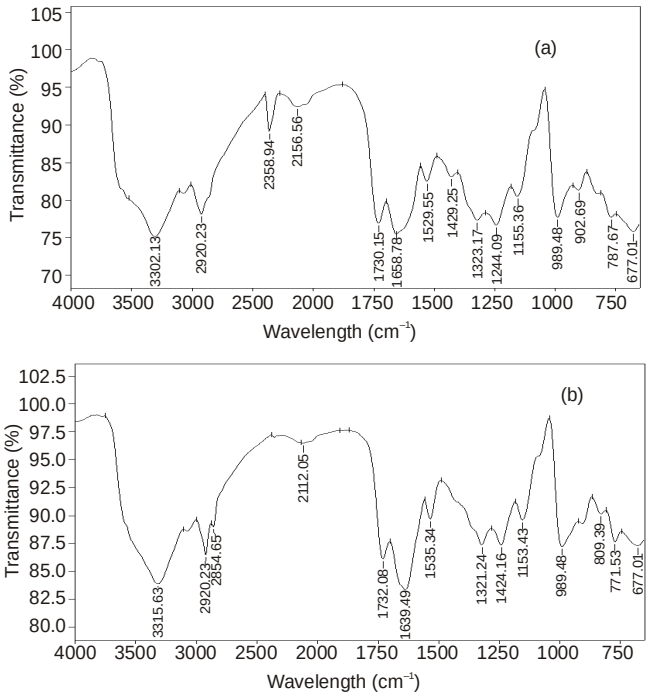

Fig. 4. FTIR spectra of formalin treated *Pisum sativum* peels (a) loaded with Alizarin yellow (b) loaded with Murexide

where C_o is initial, while C_e is the remaining concentration of dye.

Study of adsorption isotherm: Six solutions of Murexide and Alizarin yellow of different concentrations from 10-60 ppm were made by proper dilutions of stock solutions separately. In case of Alizarin yellow pH of solution was kept 3, adsorbnet dose of 0.1 g and agitate these flasks at 100 rpm for 40 min at 30 °C. In case of Murexide same process was repeated by taking the 0.3 g of the adsorbent, adjusting the pH at 3, agitate them at 100 rpm at 60 °C for 50 min. At the end, they were filtered and absorbance of filtrate was noted. Freundlich (eqn. 3), Langmuir (eqn. 4) and Temkin (eqn. 5) adsorption isotherms were plotted by using straight line equations for Murexide and Alizarin yellow and data was evaluated by using the following equations:

$$\log q = (1/n) \log C_e + \log K_F \quad (3)$$

$$\frac{1}{q} = \frac{1}{Q_{max} b}\left(\frac{1}{C_e}\right) + 1/Q_{max} \quad (4)$$

$$q = B_T \ln C_e + B_T \ln K_T \quad (5)$$

Table-1 shows the physio-chemical analysis of *Pisum sativum*. Peels of *Pisum sativum* usually consists of reactive hydrogen atoms. When treated with formalin then it goes addition reactions with reactive hydrogen atoms in *Pisum sativum* peels[18,19].

TABLE-1
PHYSICO-CHEMICAL ANALYSIS OF *Pisum sativum*

Property	Untreated *Pisum sativum* peels	Formalin treated *Pisum sativum* peels
Moisture (%)	0.06	-
pH	5.28	7.16
Carboxylic	1.37 mmol	1.41 mmol
Phenols	0.87 mmol	0.9 mmol
Lactones	0.82 mmol	0.951 mmol
Basic sites	1.33 mmol	1.38 mmol
ELEMENTAL ANALYSIS		
Macro elements (%)		
Potassium	0.098	0.0
Sodium	0.37	0.0
Calcium	0.43	0.0
Micro elements (%)		
Magnesium	0.17	0.0
Nickel	0.0	0.0
Copper	0.0	0.0
Toxic elements (%)		
Chromium	0.0	0.0
Lead	0.0	0.0
Cadmium	0.0	0.0

RESULTS AND DISCUSSION

FT-IR spectra of *Pisum sativum* peels: Fig. 3 shows the FT-IR spectrum of *Pisum sativum* peels [formalin treated peels (F.B.T.) and untreated peels] which shows different peaks to indicate the presence of complex nature of the peels. In Table-2 vibrational assignment and wave number (cm^{-1}) were given. Peaks at 3280.92, 2926.01, 1734.01, 1649.14, 1558.48, 1408.04, 1246.02, 1143.79, 80.14, 1001.06 indicate the presence of OH (alcoholic), CH (alkane), C=O, C=C, N-O, C-H, C-O (ether), C-O (alcohol), C-O (ether), =C-H (alkene), respectively. But when treated with formalin then these functional groups at different frequencies were observed. When adsorbent was loaded with Alizarin yellow and Murexide then same functional groups at different wave number and different peak shape was observed which indicated the adsorption of two dyes by the

TABLE-2
DIFFERENT FUNCTIONAL GROUPS PRESENT IN *Pisum sativum* PEELS

Untreated *Pisum sativum* peels		Formalin treated *Pisum sativum* peels	
Vibrational assignment	Wave number (cm^{-1})	Vibrational assignment	Wave number (cm^{-1})
OH (alcoholic)	3280.92	OH (alcoholic)	3292.49
CH (alkane)	2926.01	CH (alkane)	2920.23
C=O	1734.01	C≡C	2119.77
C=C	1649.14	C=O	1726.29
N-O	1558.48	C=C	1653.00
C-H	1408.04	N-O	1529.55
C-O (ether)	1246.02	C-H	1431.18
C-O (alcohol)	1143.79	C-O (ether)	1242.16
C-O (ether)	1080.14	C-O (alcohol)	1155.36
=C-H (alkene)	1001.06	=C-H (alkene)	902.69
C-Cl	769.60	C-Cl	769.60

adsorbent (Table-3). The presences of active hydroxyl groups were responsible for the adsorption of dyes[18-21].

Adsorption parameters

Adsorbent dose: Adsorbent dosage is an important factor for the determination of maximum adsorption of dyes by biosorbent. Fig. 5 shows the adsorbent dose effect for the removal of Alizarin yellow and Murexide. This graph has shown that the removal capacity of biosorbent for dyes increases with the increase of adsorbent dose. The adsorbent dose for the maximum removal of Alizarin yellow is 0.9 g/25 mL and for Murexide is 0.3 g/25 mL by using formalin treated peels. It is obvious from the results that the percentage removal of dyes increases with increase of adsorbent amount because of availability of more adsorption sites. Further increase in biosorbent after the establishment of equilibrium leads to interference between the binding sites so the percentage adsorption of dyes by biomass decreased[22].

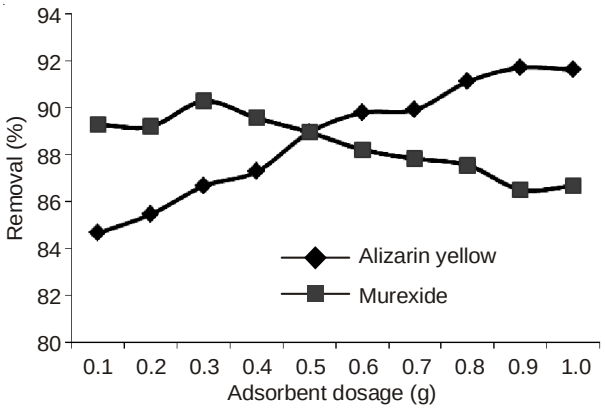

Fig. 5. Effect of adsorbent dose on percentage adsorption of Alizarin yellow and Murexide

Effect of pH: The pH of the aqueous solution was kept in the range of 3-10. Fig. 6 shows the effect of percentage adsorption of Alizarin yellow (A) and Murexide (M) by using formalin treated peels. The maximum percentage removal of Alizarin yellow and Murexide is at pH 3. So the results of experimental work show that the maximum removal is at low pH values.

This trend of adsorption of dyes at acidic pH can be understood by the structure of dyes. In case of Alizarin yellow,

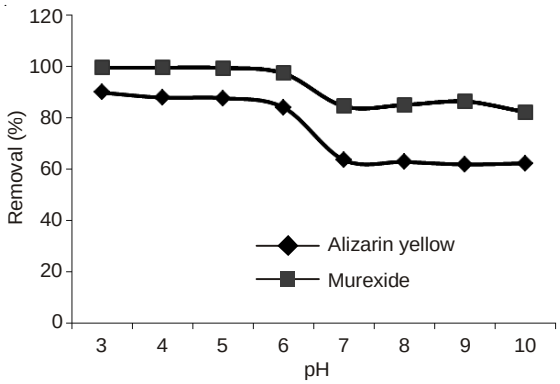

Fig. 6. Effect of pH for the adsorption of Alizarin yellow and Murexide

carboxylate and nitro groups are present (Fig. 1). In acidic pH, the adsorbents become protonated, now they having positive charge on their surface for the attraction of dye ions and hence its removal increases. But in case of basic pH, percentage removal decrease. The reason is that at high pH value negative charges accumulate on the surface of adsorbent which has repulsive effect. While in case of Murexide the reason might be for the maximum removal at acidic pH is due to presence of attractive forces like hydrogen bonding between formalin treated peels and dye ions[23].

Effect of time: It has been reported that time is an important factor for biosorption. Fig. 7 shows that the maximum adsorption of Alizarin yellow is 88.91 % at the contact time of 40 min and for Murexide is 90.53 % at 10 min. The above results show that the adsorption capacity of biomass increases with the increase of time. The reason is that the more time is available for dyes to come in contact with the biomass. So the initial removal of dyes occur immediately because more sites are available but after the optimum time, decrease in adsorption capacity of biomass take place because all the sites are occupied and no more sites are available.

Effect of temperature: It is observed from the experimental results that temperature is an important factor which significantly affects adsorption process. Different modes of adsorption were studied by varying temperature from 20 to 80 °C. Fig. 8 shows the comparative effect of temperature on dyes. It shows that maximum percentage removal of Alizarin yellow is 88.37 % at 30 °C and for Murexide is 95.17 % at 60 °C. The results show that adsorption process increases with

TABLE-3
CHANGED VALUES OF WAVE NUMBER (cm^{-1}) FOR FORMALIN TREATED PEELS (F.T.B) WHEN UNLOADED, LOADED WITH ALIZARIN YELLOW AND LOADED WITH MUREXIDE

Vibrational assignment	Wave number (cm^{-1})		
	Unloaded adsorbent (F.T.B)	F.T.B loaded with alizarin yellow	F.T.B loaded with Murexide
OH (alcoholic)	3292.49	3302.13	3315.63
CH (alkane)	2920..23	2920.23	2920.23
C≡C	2119.77	2125.56	2112.05
C=O	1726.29	1730.15	1732.08
C=C	1653.00	1658.78	1639.49
N-O	1529.55	1529.55	1535.34
C-H	1431.18	1429.25	-
C-O (ether)	1242.16	1244.09	1242.16
C-O (alcohol)	1155.36	1155.36	1153.43
C-H (alkene)	902.69	989.84	989.48
C-Cl	769.60	767.67	771.53

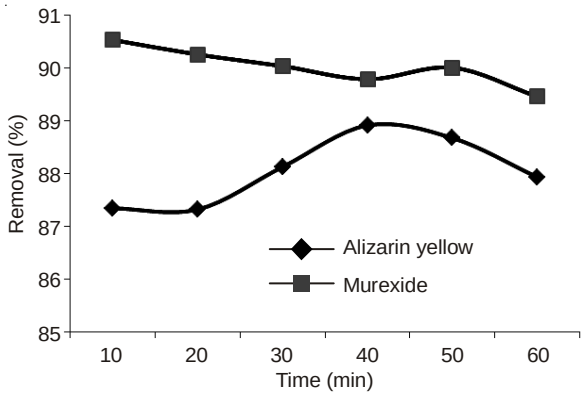

Fig. 7. Effect of contact time on percentage removal of Alizarin yellow and Murexide

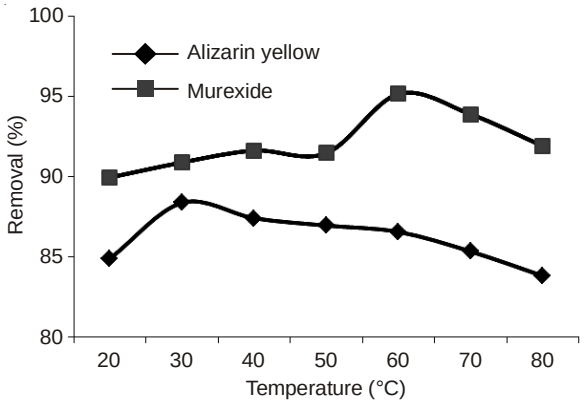

Fig. 8. Effect of temperature for the percentage removal of Murexide and Alizarin yellow

increase in temperature in case of Murexide but after gaining the optimum temperature adsorption becomes constant or decreases. While in case of Alizarin yellow the maximum removal at 30 °C and after this temperature removal of dye decreases. The reason may be that at high temperatures molecules move faster and less time is available for interaction with biomass.

Effect of agitation rate: It has been reported that agitation speed affects the adsorption process greatly. Fig. 9 indicated the comparative effects of agitation rate on dyes adsorption. It shows that maximum removal of Alizarin yellow is 86.73 % and for Murexide is 91.42 % at 100 rpm.The above results show that adsorption rate increases with the increase of agitation speed. The reason is that at low speed of agitation, adsorbent accumulated in the sample solution of dyes instead

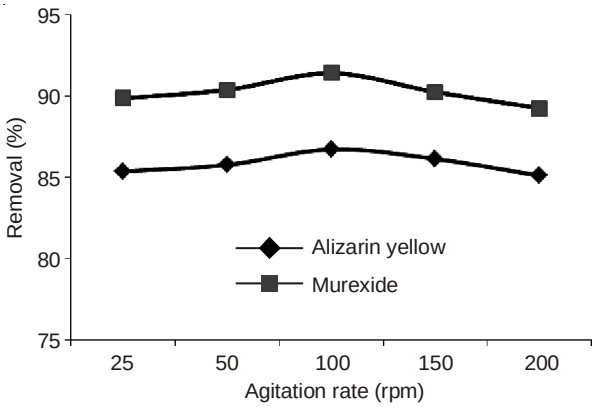

Fig. 9. Effect of agitation rate for the removal of Alizarin yellow and Murexide

of spreading. So various active sites buried under the above layer. Dyes will be adsorb on the above layer of adsorbent and lower buried active sites are not available hence removal just takes place on the above layer. So the agitation rate should be optimum so that all the active sites are available for dye uptake[23].

Adsorption isotherm: Freundlich adsorption isotherm indicated the physiosorption on heterogeneous surface in a multi layer pattern. Langmuir model tells us about the mono-layer chemisorption, while Temkin model indicates indirect adsorbent-adsorbate interaction. Isothermal parameters are evaluated from the eqns. 3, 4 and 5 Freundlich, Langmuir and Temkin model. Fig. 10 shows Freundlich isotherm for both dyes and parameters were given in Table-4. The R^2 value for Freundlich isotherm was 0.994 in case of Alizarin yellow and 0.955 in case of Murexide. The value of K_F was 0.09 for

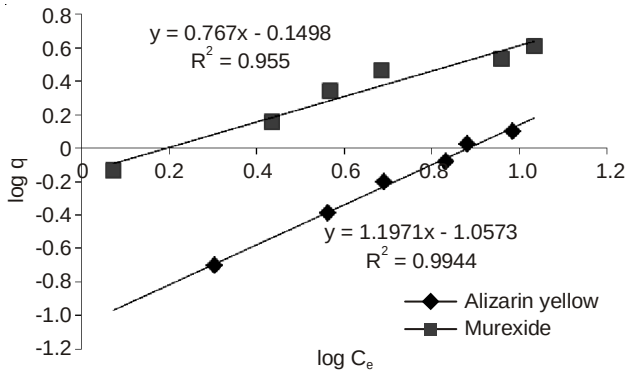

Fig. 10. Freundlich adsorption isotherm for Murexide and Alizarin yellow

TABLE-4
FREUNDLICH ISOTHERM PARAMETERS

	Freundlich Isotherm Parameters				
Dye	Slope	Intercept	R^2	K_F	n
Alizarin yellow	1.197	-1.057	0.994	0.09	0.835
Murexide	0.767	-0.150	0.955	0.71	1.304

TABLE-5
LANGMUIR ISOTHERM PARAMETERS

Dyes	Langmuir Isotherm Parameters				
	Slope	Intercept	R^2	Q_{max} (mg/g)	b
Alizarin yellow	2.175	0.406	0.959	2.47	0.186
Murexide	1.504	0.091	0.989	11.04	0.060

TABLE-6
TEMKIN ISOTHERM PARAMETERS

Dyes	Temkin Isotherm Parameters				
	Slope	Intercept	R^2	K_T	B_T (KJ/mol)
Alizarin yellow	0.679	-0.379	0.941	0.68	-0.379
Murexide	1.512	0.292	0.958	1.51	0.292

Alizarin yellow and 0.71 for Murexide. K_F is ultimate adsorption capacity. Fig. 11 shows Langmuir isotherm for two dyes and corresponding parameters are given in Table-5. The correlation coefficient value is 0.959 for Alizarin yellow and 0.989 for Murexide. The value of Q_{max} is 2.47 for Alizarin yellow and 11.04 mg/g for Murexide. Fig. 12 shows Temkin isotherm for both dyes and Table-6 shows its parameters. R^2 value is 0.941 for Alizarin yellow and 0.958 for Murexide, B_T value (heat of sorption) was calculated for Alizarin yellow is 0.379 KJ/mol. The correlation coefficient values shown that Freundlich adsorption isotherm was best fitted for the removal of Alizarin yellow (A) and Murexide (M).

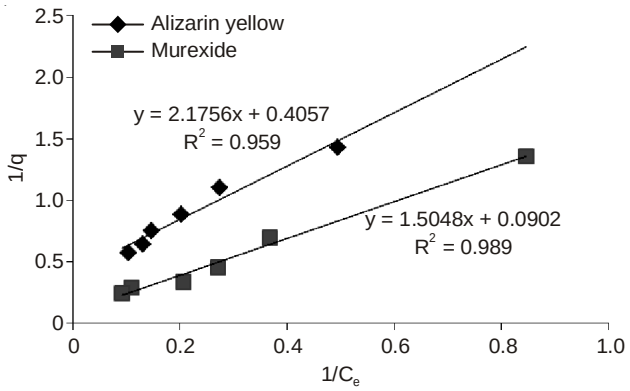

Fig. 11. Langmuir adsorption isotherm for the removal of two dyes

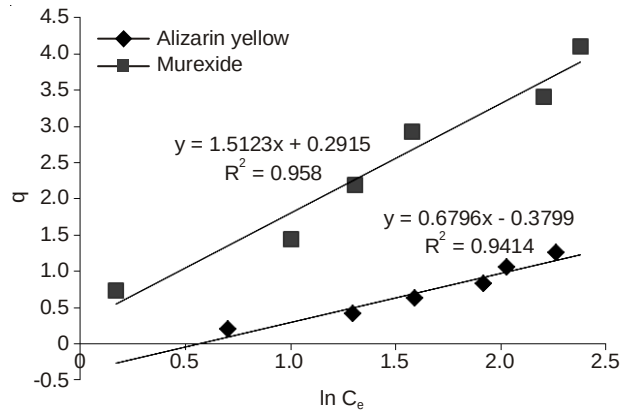

Fig. 12. Temkin adsorption isotherm for Alizarin yellow and Murexide

Conclusion

All the experimental results indicate that dried peels of *Pisum sativum* are eco-friendly and low cost biosorbents for the removal of harmful dyes from textile effluents that are discharged in water and hence contaminate the water. *Pisum sativum* peels have good adsorptive properties for Alizarin yellow and Murexide due to their large surface area, porosity and type of adsorbing sites, *etc*. In this research work, the relatively shorter contact time, acidic pH value, endothermic nature of biosorption was found for the maximum removal of dyes from wastewater.

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