Removal of Anionic dye from Industrial Effluents with Raw and Chemically Modified Chickpea Husk

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Summary: Alizarin Red S is an industrial dye commonly used for dyeing the fabric in textile industry. In present work the parameters to remove this dye from aqueous media by adsorption on raw as well as chemically modified chickpea husk have been investigated. Besides checking the effects of concerned parameters like time of contact, dose of adsorbent, pH, speed of agitation and temperature, for both raw and zinc modified chickpea husk were characterized for functional groups by FTIR spectroscopy. To investigate the adsorption mechanism, Langmuir, Freundlich and Temkin isotherms were plotted. Kinetic and thermodynamic studies were also performed to understand the nature of adsorption process. Chickpea husk proved itself as an effective and cheap bio-adsorbent, which is easily available in abundance at indigenous level. When treated with zinc chloride the removal efficiency of chickpea increased more than two folds.

Keywords: Dyes, Adsorption, Chickpea husk, Isotherms.

Introduction

Water pollution is one of the major problems that various countries of the world are facing today. Around 98% of water on earth is seawater. Fresh water comprises only 2% of water. 1.6% of the water is secured in the polar ice caps and glaciers. Another 0.36% is present underground in wells and aquifers. Just around 0.036% of the total water on earth is found in streams and lakes. Drinking water is contaminated by the natural sources but the prominent sources of water pollution are anthropogenic. Industry in developing countries is one of the major sources of water pollution. Tons of toxic chemicals are daily used for various purposes in different industries but then a significant quantity of these chemicals is washed out untreated or poured into nearby water streams, ponds and lakes. This polluted water is sometimes directly used for irrigation or left free to seep down into earth to mix with ground water. As a result of this water borne diseases are increasing at alarming rate in countries like Pakistan.

Textile industry is one of the major industries in cotton growing countries. The textile industry is the largest industry in Pakistan. At present, there are more than two thousand textile units, which are producing various types of fabrics both for export as well as local market. A large number of synthetic dyes are used in the dyeing units of these textile industries. Large quantities of water are needed for textile processing, dyeing and printing. Among these various processes, dyeing process includes fixing dyes on fabrics, washing etc requires more water [1] and it consumes 16% of total water usage depending on the type of dyes used and this dyeing sector contributes to 15% - 20% of the total waste water flow. According to WHO nearly 80% of water is polluted in developing country due to the dumping of domestic waste into aquatic bodies. Particularly in India almost 70% of the water has become polluted due to the discharge of domestic sewage and industrial effluents into natural water source, such as rivers, streams as well as lakes [2]. After the dyeing process, most of these dyes when discharged through effluents in water pose severe risk to human lives, due to their carcinogenic and mutagenic in nature. Even in dissolved form these dyes are stable to heat and light and usually non-degradable due to their chemical structure. Hence treatment of wastewater is very important before its discharge. Basically three types of methods are used for treating the wastewater from an industry: physical; chemical and biological. Biological methods are not effective for removing dyes from wastewaters. Chemical methods need very expensive chemicals and sophisticated procedures. Sludge removal may also a major issue in these methods. Physical methods include sedimentation, distillation, coagulation and adsorption. Among these methods adsorption has become most effective technique for removal of textile dyes due to its cost effectiveness, efficiency, sludge free operation and simplicity [3]. This technique becomes ideal when carried out through an indigenous, cheap and easily available

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adsorbent. As reported in literature a large number of adsorbents have been investigated for removing different dyes from industrial effluents [4]. Alizarin Red S ($C_{14}H_7O_7SNa$) is widely used water soluble anthraquinone dye and is synthesized from the natural alizarin dye by sulfonation. Structure of alizarin red S is shown in Fig. 1.

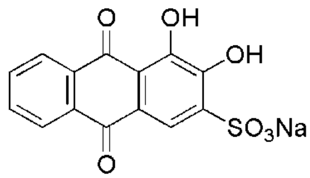

Fig. 1: Structure of Alizarin Red S.

In addition to textile dyeing it is used for staining, fluorine determination, chemical mechanical polishing and as an acid-base indicator. Alizarin Red S is poisonous dye, it was previously removed by the use of mustard husk [5], Lantana camara [6], Cyanodon dactylon [7], activated charcoal [8], and activated carbon prepared from coconut shell [9].

In present work Alizarin Red S has been removed from aqueous media with chickpea husk as adsorbent. Chickpea husk is easily available from the local market. Usually it is thrown away as a waste from industry when it is separated from a seed of chickpea. It is also used as food for animals and as fire wood in public cafeterias and hotels etc. [4]. In present work chemical modification of chickpea husk has been done in order to increase its surface area and adsorption capacity. Zinc chloride is employed for chemical modification of raw husk. Literature reported that activation with zinc chloride increased the surface area of adsorbent [10]. Activation of different adsorbents for the removal of metal ion has been practiced but a little attention has been focused for the removal of anionic dyes using such simply treated adsorbents. The adsorbent selected for this study proved effective in removing this toxic dye from water and use of such adsorbents in underdeveloped countries like Pakistan for water decontamination can help to avoid various water borne diseases. Use of zinc chloride for treating chickpea husk in this work was based upon the idea to select such treating reagent that imparts no harmful effects to human health.

Experimental

Reagents

Most of the reagents used in this work were of AnalaR grade. Alizarin Red S (Sodium Alizarin sulfonate) stock solution (1000 mg L^{-1}) was prepared by dissolving 1g of the dye in distilled water. All the working solutions were prepared freshly by diluting the stock solution. Solutions of NaOH (~0.1M) and HCl (~0.1M) were also prepared by dissolving appropriate amounts in distilled water.

Instruments used

The absorption studies of Alizarin Red S were carried out by using UV-Visible Spectrophotometer (HITACHI U-1800) at wavelength 423nm. For pH measurements pH meter (WTW T20) was used.

Adsorbent preparation

Chickpea husk purchased from a local market of Lahore, Pakistan. In order to make it free from dust particles, it was washed with distilled water and dried in an oven for two hours to remove moisture. Later the mass was grinded into fine powder form and sieved through 60 mesh (ASTM). The ground mass was stored in airtight glass jars. This was designated as raw chickpea husk (RCPH). 100 grams of raw husk was mixed with zinc chloride in a ratio 1:2 and is exposed to microwaves for 5 minutes. This mixture was then boiled in water for 20 minutes and filtered. The residue was washed with warm deionized water to remove excess of zinc chloride from the adsorbent. After that the residue was dried in oven till it become moisture free. This was designated as zinc chloride modified chickpea husk (ZMCPH) and used for further experiments. Procedure for the modification of the adsorbent with the different modifying reagent was used for Cr (III) removal using sorghum biomass [11].

Procedure

A known weight of raw or modified adsorbent was added to 50ml of 25ppm solution of Alizarin Red S (ARS) dye in a 50ml conical flask. The contents were shacked for a known time at a given temperature. After the experiment the contents were filtered and absorption of the filtrate was measured at 423nm. Concentration of the dye was calculated from an absorption-concentration calibration graph. Percentage removal and adsorbed quantity of Alizarin Red S (q_e) calculated from following equation:

$$\%age\ removal\ of\ Alizarin\ Red\ S = \frac{C_o - C_e}{C_o} \times 100 \quad \text{eq.1}$$

$$q_e = \frac{(C_o - C_e)V}{M} \quad \text{eq.2}$$

where

C_o = initial Alizarin Red S concentration (mg L^{-1})
C_e = Equilibrium concentration of ARS (mg L^{-1})
M= Mass of adsorbent
V= Volume of solution (L)
q_e= quantity of Alizarin red S adsorbed

Results and Discussion

Treatment of industrial wastewater is a critical issue of environmental pollution. Discharge from textile industry usually consists of dyes and other organic substances. Dyes are the class of pollutants that are highly toxic as well as stable and non-degradable. In this study model experiments were carried out to adsorb a common dye Alizarin Red S from aqueous media by an economical, and ecofriendly adsorbent chickpea husk. Various parameters affecting the adsorption have been investigated. The experiments were carried out on raw husk as well as on modified with zinc chloride. It has been noticed that the removal efficiency increased almost three times when modified chickpea was used. Adsorption mechanism was investigated by plotting various isotherms. Kinetic studies and thermodynamic studies also helped in exploring the nature of binding the dye on adsorbent surface.

Effect of Contact time

Contact time is a very important factor in attaining the adsorption equilibrium. In these studies time interval was varied from 2 to 80 minutes. In case of RCPH the maximum adsorption took place in first 5 minutes. After that a slight decrease was noticed in the removal of the dye by the adsorbent. This was probably due to the fact that adsorption sites became saturated in first five minutes and in longer intervals the dispersion of dye molecules in solution started again. However in case of the ZMCPH, it took 25 minutes to reach at maximum adsorption and then a slight depression in adsorption was observed. It revealed that bonding between dye and adsorbent in the presence of zinc ions is more effective as compared to the bonding in untreated form. The influence of contact time on % age removal efficiency of RCPH and ZMCPH is shown in Fig. 2.

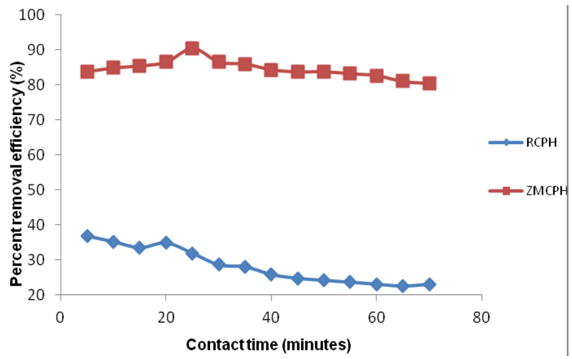

Fig. 2: Effect of Contact Time on removal efficiency of RCPH (raw) and ZMCPH (zinc modified).

Adsorbent Dose: 0.5g, Shaking Speed: 150rpm, Solution concentration: 25ppm/50mL

Effect of Agitation Speed

Removal efficiency of RCPH as well as ZMCPH was checked by varying the agitation speed from 50 to 450 rpm while the contact time was kept 5 minutes and 25 minutes respectively. In case of raw adsorbent the maximum adsorption was found at 150 rpm while modified husk adsorbed maximum dye at 100 to 150 rpm. At 150 rpm the removal efficiencies of raw and modified husk were 33.5% and 78% respectively. After that the percentage removal efficiency starts decreasing slightly by further increase in agitation speed. This is due to the increase in kinetic energy and collision which cause the detachment of loosely bonded dye ions. The influence of agitation speed on % age removal efficiency of RCPH and ZMCPH is shown in Fig. 3.

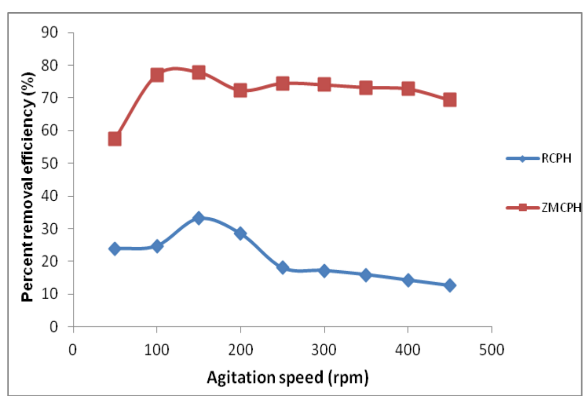

Fig. 3: Effect of Shaking Speed on removal efficiency of RCPH (raw) and ZMCPH (zinc modified).

Adsorbent Dose: 0.5g, contact time: 30min, Solution concentration: 25ppm/50ml, Temperature: 293K

Effect of Adsorbent dose

It is evident from the Fig. 4 that percentage removal efficiency of raw and modified husk increased with increase in the adsorbent dose and reached at its maximum removal efficiency of 39.62% and 96.70% at 0.3g and 0.7g respectively, which is due to the availability of binding sites. After that in case of raw husk it starts decreasing slightly which was probably due to the saturation of binding sites and remains constant in case of modified husk due to further unavailability of dye for adsorption onto available binding sites. The effect of adsorbent dose was checked at optimum contact time for each type of the adsorbent.

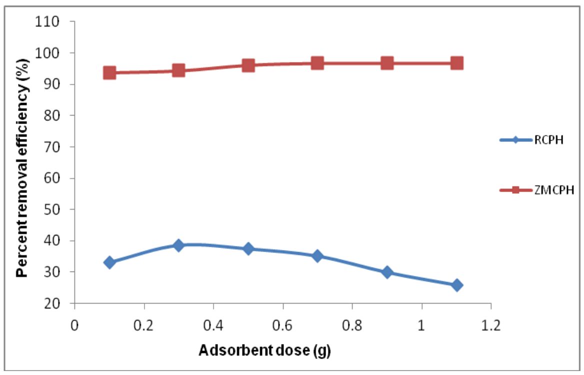

Fig. 4: Effect of Adsorbent Dose on removal efficiency of RCPH (raw) and ZMCPH (zinc modified).

Shaking Speed: 150rpm, Contact Time: 5 mints for RCPH and 25 mints for ZMCPH, Solution concentration: 25ppm/50mL

Effect of Temperature

To check the effect of temperature on dye adsorption, temperature was varied from 20 to 60°C. In both the cases, raw husk and modified husk, maximum adsorption was observed at 30°C. This was probably due to the fact that at this temperature equilibrium exists in favor of maximum adsorption on available sites. After this critical temperature equilibrium shifts in the favor of dye molecules dispersed in solution. Fig. 5 reveals that the percentage removal of Alizarin Red is a function of temperature in the range 10-60°C for raw and modified husk.

Effect of Solution pH

In adsorption process, solution pH is an important factor. pH not only determines the solubility of dye but also affect the functional groups at the adsorbent surface. Fig. 6 reveals that percentage removal efficiency of RCPH and ZMCPH increased up to pH 4 and 5 respectively due to the binding of negatively charged dye ions to the adsorbent surface containing positively charged functional groups through electrostatic forces of attraction. Above pH 4 and 5, the percentage removal efficiency starts decreasing which is due to the unavailability of positively charged functional groups onto adsorbent surface. As a result anionic dye repelled by positively charged adsorbent surface [10]. The effect of pH on the process of adsorption can be further studied through the pH_{zpc} (zero point charge) the point at which adsorbent contains zero charge. In this study pH_{zpc} of RCPH was determined and that is 5.76. This shows that $pH<pH_{zpc}$ and the surface of adsorbent is positively charged which favors the adsorption of anionic dye Alizarin Red S.

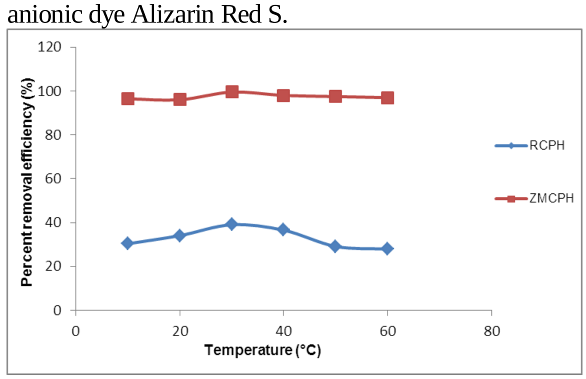

Fig. 5: Effect of Temperature on removal efficiency of RCPH (raw) and ZMCPH (zinc modified).

Adsorbent Dose: RCPH=0.3g and ZMCPH=0.7g, Shaking Speed: 150 rpm, Contact Time: RCPH=25 min and ZMCPH=5 min

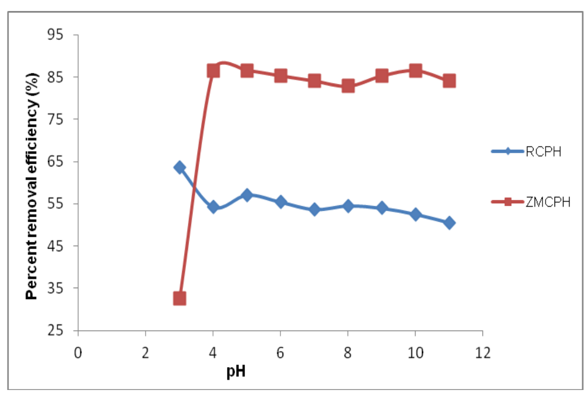

Fig. 6: Effect of pH on removal efficiency of RCPH and ZMCPH.

Adsorbent Dose: RCPH=0.3g and for ZMCPH=0.7g, Shaking Speed: 150 rpm, Contact Time: RCPH=25 min, ZMCPH=5 min

`Adsorption Isotherms

Isotherms are employed to describe the mechanism of adsorbent-adsorbate interaction. Various isothermal models were used to analyze equilibrium parameters and relationship between C_e (equilibrium concentration, mg L^{-1}) and q_e (adsorbed quantity at equilibrium, mg g^{-1}) but in this study we used Langmuir, Freundlich and Temkin isotherms to investigate the nature of interaction between the dye and the adsorbent.

Langmuir isothermal equation is as follows:

$$\frac{1}{q_{eq}} = \frac{1}{b\, q_{max}\, C_{eq}} + \frac{1}{q_{max}} \quad \text{eq.3}$$

where q_{eq} (adsorption capacity, mg g^{-1}), C_e (concentration of adsorbate at equilibrium mg L^{-1}), q_{max} (maximum adsorption capacity) and b (Langmuir isotherm constant Lmg^{-1}). It represents the homogeneous adsorption.

The Freundlich isothermal model is signified as follows:

$$q_e = K_f\, C_e^{\frac{1}{n}} \quad \text{eq.4}$$

where K_f (equilibrium constant of adsorption) and n (heterogeneity factor related to adsorption intensity and capacity). It represents the multilayer adsorption heterogeneous surfaces of adsorbents.

Temkin isotherm has been explained by the following equation:

$$q = \frac{R_T}{B_T} \ln K_T\, C_e. \quad \text{eq.5}$$

where 'K_T' is Temkin isotherm constant and 'B_T' is Temkin factor related to heat of adsorption.

The parameters and correlation coefficients obtained from the adsorption of ARS are given in Table-1. The value of R^2 in all cases is approaching unity but the adsorption data is best fitted to Langmuir isotherms where higher R^2 value indicated that the homogeneous adsorption predominated in the case of ARS adsorption onto the surface of chickpea husk. Furthermore, the adsorption capacity for RCPH and ZMCPH was 5.853 and 39.30 mg/g respectively. Favorability of the process is shown by value of R_L. In the existing study R_L values for RCPH and ZMCPH were 0.727 and 0.645 respectively which clearly indicated the favorability of the adsorption process. Higher adsorption capacity values clearly revealed that zinc modification effectively increased the surface adsorption capacity of chickpea husk. Adsorption capacity of ZMCPH is comparable to the adsorbents reported in literature for the removal of ARS as tabulated in Table-2.

Value of 'n' calculated for RCPH was found to be 0.882, representing average adsorption and for ZMCPH was 1.125 indicated good adsorption. 'B_T' values for adsorption of ARS on RCPH was 6.260 $KJmol^{-1}$ indicating moderately weak cohesive forces between the dye and the RCPH whereas, in case of ZMCPH this value was 2.029 $KJmol^{-1}$ indicating the strong cohesive forces between adsorbent and the dye.

Thermodynamic Studies

The thermodynamic parameters such as changes in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated from equations

$$\Delta G^\circ = -RT\ln K_D \quad \text{eq.6}$$

Here 'R' is the universal gas constant (8.3134 $Jmol^{-1}K^{-1}$) and 'T' is the absolute temperature of the medium in Kelvin. 'K_D' represents the distribution coefficient for the adsorption and it can be calculated from equation;

$$K_D = C_0 - C_e / C_e \quad \text{eq.7}$$

C_e is the concentration (mg/L) of Alizarin Red S at equilibrium.

$$\ln K_D = (\Delta S^o/R) - (\Delta H^o/RT) \quad \text{eq.8}$$

Enthalpy and entropy for adsorption of ARS was calculated by the regression analysis of linear plots of In K_D vs. 1/T and then used for calculating ΔG° values as mentioned in equation 9;

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{eq. 9}$$

All these parameters are shown in the Table-3. Negative values of ΔG° showed the spontaneous nature of adsorption of dye onto both adsorbents, whereas the negative value of ΔH° showed the exothermic nature of adsorption process in case of RCPH and positive value of ΔH° showed the endothermic nature of adsorption process for ZMCPH. Positive value of entropy ΔS° showed that when dye is adsorbed on the surface of RCPH and ZMCPH the binding forces imparted randomness to the system.

Table-1: Langmuir, Freundlich and Temkin parameters for RCPH and ZMCPH.

Adsorbents	Langmuir				Freundlich			Temkin		
	B (L g^{-1})	Q_{max} (mg/g)	R_L	R^2	n	K_F (L/g)$^{1-n}$	R^2	B_T (KJmol^{-1})	K_T (mg g^{-1})	R^2
RCPH	0.015	5.853	0.727	0.949	0.882	0.036	0.953	6.260	0.416	0.871
ZMCPH	0.262	39.30	0.645	0.981	1.125	1.168	0.970	2.029	3.351	0.897

Table-2: Comparison of adsorption capacities of various adsorptions for ARS.

Adsorbents Used	Dye	Adsorption Capacity (mg/g)	References
Mustard Husk	Alizarin Red S	1.97	[5]
Cynodon dactylon	Alizarin red S	16.32	[7]
Activated clay modified by iron oxide	Alizarin red S	32.7	[13]
RCPH	Alizarin red S	5.853	Present work
ZMCPH	Alizarin red S	39.30	Present work

Table-3: Thermodynamics parameters for raw (RCPH) and zinc modified (ZMCPH) chickpea husk.

Adsorbents	Temperature (K)	ΔG^0 (KJ mol^{-1})	ΔH^0 (KJ mol^{-1})	ΔS^0 (KJ mol^{-1})
RCPH	283	-7.7625	-7.666	0.103
	293	-7.8718		
	303	-7.9539		
	313	-8.1378		
	323	-8.1668		
	333	-8.2707		
ZMCPH	283	-0.10166	0.249	0.260
	293	-0.24966		
	303	-0.46484		
	313	-0.69103		
	323	-0.10799		
	333	-1.37887		

The negative value of ΔG^0 for the removal of dye by treated husk at studied temperature range demonstrates that the process was thermodynamically feasible and would be a spontaneous one. Also, the increase in negative value of ΔG^0 with the increase in temperature describes that the process was exothermic in nature. The negative value of ΔH^0 for ZMCPH showed that the adsorption of Alizarin dye was exothermic. The positive value of ΔS^0 for the adsorbent showed the randomness at the solid-solution interface during the adsorption process reflecting the ability of adsorbent for the dye. [7].

Kinetic Study

The adsorption process depends upon the mass transport process and also on physical and chemical characteristics of the adsorbent. Various kinetic models are used to explain the kinetics mechanism but here two models were employed i.e. pseudo first order kinetics model and pseudo second order kinetics model as represented by the following equations:

Pseudo first order equation

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303}t \quad \text{eq.9}$$

Pseudo second order equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad \text{eq.10}$$

where K_1 is Pseudo first order rate constant, K_2 is Pseudo second order rate constant, q_e is quantity adsorbed at equilibrium and q_t is the quantity of dye adsorbed at any time.

In order to find out the applicability of kinetics models, the correlation coefficient (R^2) was calculated. Results are tabulated in Table-4. In case of Pseudo second order model the R^2 value for raw and modified husk is approaching to unity which clearly indicates the applicability of Pseudo second order kinetics. Value of correlation coefficient approaching unity revealed the effect of mass transfer on initial diffusion of dye into pores of the adsorbent as well as the intraparticle diffusion of the dye [11, 12].

Characterization of Adsorbent by FTIR

In order to determine the functional groups present on adsorbents surface, FT-IR analysis of RCPH and ZMCPH were done and represented in Fig.7 and 8. Characteristics adsorption frequencies of various bands given in Table-5.

Table-4: Kinetics parameters values for raw (RCPH) and zinc modified chickpea husk (ZMCPH).

Adsorbents	Pseudo First order			Pseudo Second order		
	q_m (mg g^{-1})	K_1 (min^{-1})	R^2	K_2 (min^{-1})	q_m (mg g^{-1})	R^2
RCPH	0.004	0.059	0.877	0.143	4.128	0.998
ZMCPH	0.054	0.008	0.991	0.184	11.158	0.999

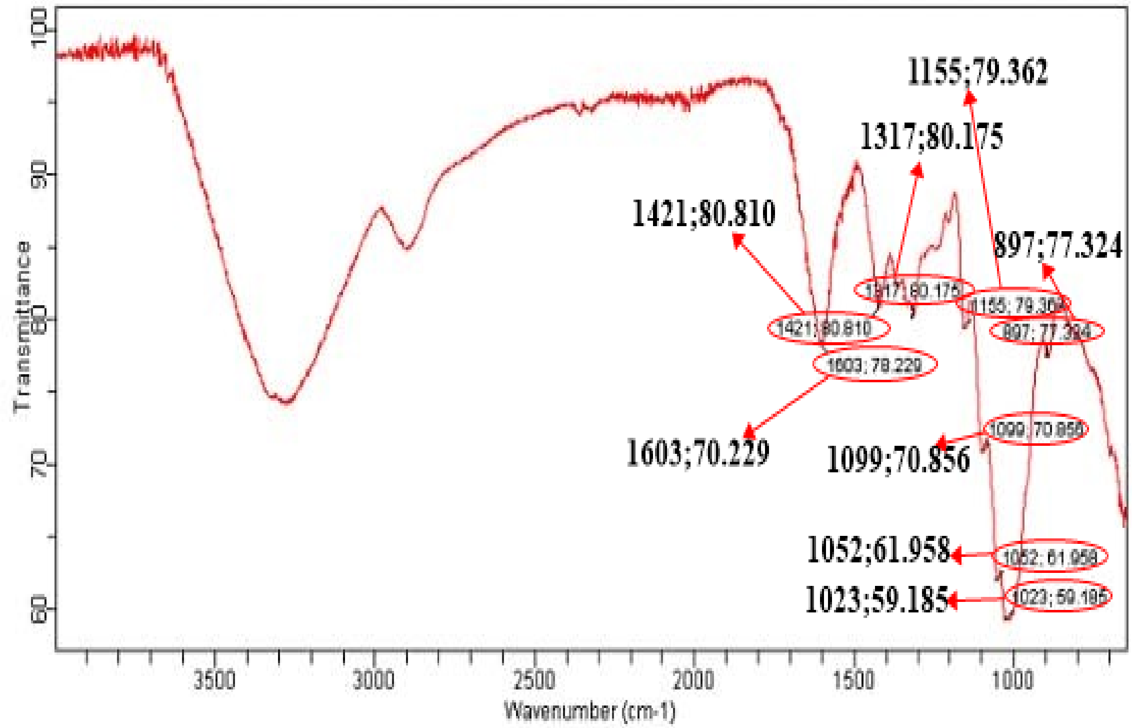

Fig. 7: FT-IR spectra of raw chickpea husk (RCPH).

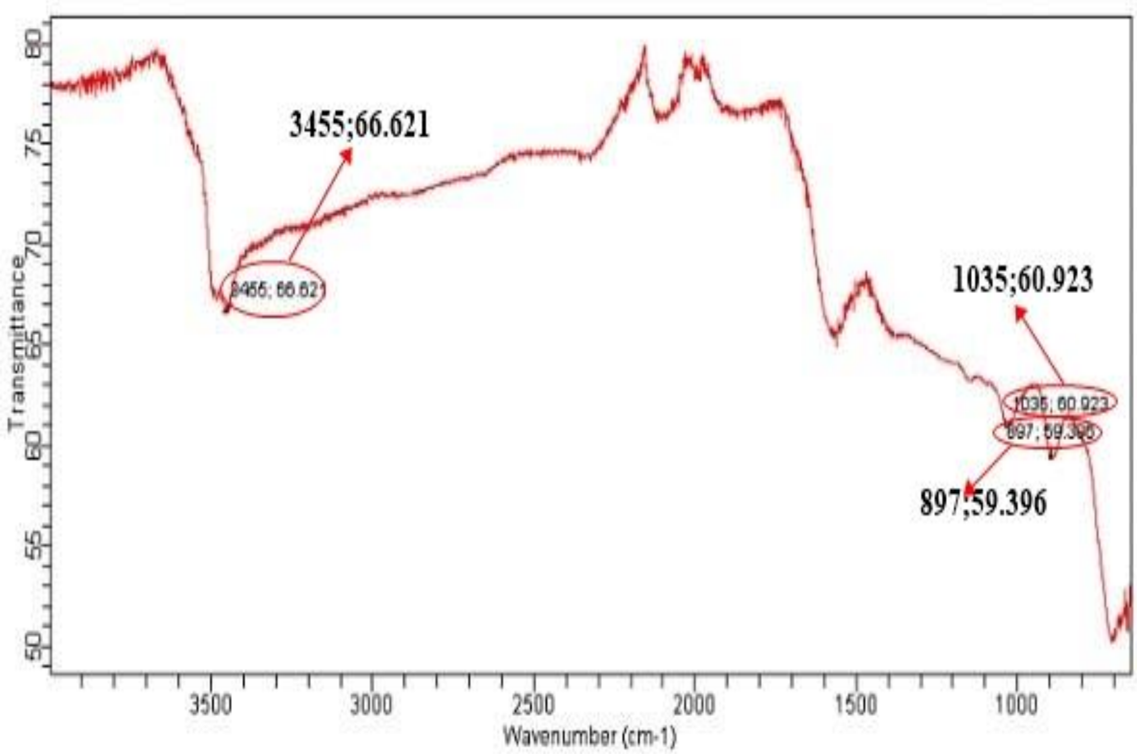

Fig. 8: FT-IR spectra of zinc modified chickpea husk (ZMCPH).

Table-5: Characteristics FT-IR band absorption frequencies of RCPH and ZMCPH.

Functional group characteristics absorption band (cm^{-1})	Adsorbent sample	
	RCPH	ZMCPH
ν (N-H) stretching of primary amines and secondary amines, amides (3400-3250) bending (1650-1580)	1603	3455
ν (C-H) bending of alkanes (1480-1350) ν (C=C) of aromatic rings (1600-1400)	1421	-
ν (C-N) stretching of aromatic amines (1335-1250) ν (C=O) stretching of alcohols, carboxylic acids, esters, ethers (1320-1210)	1317	-
ν (C-N) stretching of aliphatic amines (1250-1020)	1155	1035
ν (C=O) stretching of esters (1300-1000)	1099 1052 1023	
ν (=C-H) bending of alkenes (1000-650) ν (N-H) wagging of primary and secondary amines (910-665)	897	897

It can be easily seen that the functional groups that became the active sites for adsorption was amines and amides and adsorption of dye increased after chemical treatment of raw adsorbent. These changes were due to the activation of positively charged amide group on surface of ZMCPH. This positively charged functional group adsorbed the dye firmly through electrostatic forces of attraction as the dye is anionic in nature and in solution it is present with the negative charge on it.

Conflict of Interest

There exists no conflict among the authors regarding the publication of this work.

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