Removal of Methyl Orange from Textile Waste Water Using Nanochitosan, Starch, Polyacrylamide Ternary Blend with and without Glutaraldehyde

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Abstract

The removel of methyl orange(MO) from textile industries has been investigated using Nanochitosan (NCS)/ Starch (S) binary blend using of with and without cross linking agent(Glutaraldehyde) under different experimental conditions of initial concentration, adsorbent dose, contact time, and pH using Batch adsorption method. The adsorption data has been explained in terms of Langmuir, and Freundlich equations. The sorption kinetics was tested for the pseudo first order and pseudo second order reactions. The results revealed that the adsorptions of methyl orange onto Nanochitosan/Starch blend was found to fit well with the Langmuir and Freundlich isotherm.The rate constants of sorption for kinetic models were calculated and good correlation coefficients obtained for the pseudo second order kinetic model.The results indicate that under the optium conditions the Nanochitosan/Starch binary blend using of with and without cross linking agent(Glutaraldehyde) was found as an effective adsorbent for methyl orange.

Key words: NAC: Nanochitosan, S: Starch, MO: Methyl orange, Adsorbtion, Isotherm

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Introduction

Water pollution is one of the most undesirable environmental problems in the world and it requires solutions. Textile industries produce a lot of wastewater, which contains a number of contaminants, including acidic or caustic dissolved solids, toxic compounds, and any different dyes, Many of the organic dyes are hazardous and may affect aquatic life causing various diseases and disorders.[1] Synthetic dyes are extensively used in various branches of the textile industry, paper printing, color photography, pharmaceutical, leather, cosmetics, plastic, and other industries. The discharges of industrial wastewater containing dyes cause a real environmental problems because of its high toxicity and possible accumulation in the environment[2, 3].

Synthetic dyes are a group of most dangerous pollutants in water. [4-6] The presence of even very low concentrations of dyes in water reduces light penetration through the water surface, precluding photosynthesis of the aqueous flora.[7] Many of these dyes are carcinogenic, mutagenic, and teratogenic and also toxic to human beings, fish species , and microorganisms. Hence, their removal from aquatic wastewater becomes environmentally important.[8] A great variety of synthetic dyes are produced on a daily basis in dyestuff, textile, leather, paper and food industries[9].

Dyes are natural or synthetic colorants used in various industries such as textiles, tanneries, paints, pulp and paper. Even if a small amount of dye is present in water (for example, even less than 1 ppm for some dyes), it is highly visible and therefore undesirable [28]. During the dyeing process, 10 to 15% of the dye is lost in the effluent [27]. Effluents discharged from dyeing industries are highly colored and are toxic to aquatic life in the receiving water bodies. Some dyes are carcinogenic which require separation and advanced treatment before being discharged into conventional systems. Based on the chromophore group, 20 to 30 different groups of dyes can be discerned. Dyes may be classified according to chemical constituents, application class and end use. Azo, monoazo, diazo, nitro, azine, thioazine, anthroquinone, quinoline, sulphur, xanthene, phthalocyanine and nitoros are classification of dyes based on their chemical constituents. Based on their applications, dyes are classified as acid dyes, basic dyes, direct dyes, mordant dyes, vat dyes, reactive dyes, disperse dyes and sulfur dyes. There are many structural varieties of dyes that fall into either the cationic, nonionic or anionic type.

Some natural biomaterials including agricultural products and other by-products with low costs have been explored as new sources in recent years. Thus, dye removal by agricultural by-products and other low cost sorbents has also been intensively investigated. Materials deriving from agricultural by-products can be useful to convert unwanted, surplus agricultural waste, of which billions of kilograms are produced annually, into a useful adsorbent, a value-added advantage[1]. Many specific examples are found where disposal of agricultural by-products has become a major, costly waste disposal problem[10].

Currently, there are several treatment technologies used in the removal of dyes from waste effluents such as electrochemical treatment, coagulation, precipitation, solvent extraction, membrane filtration and advanced oxidation process[10]. Activated carbon, a widely used adsorbent in industrial processes, is composed of a microporous, homogenous structure with high surface area and shows radiation stability[11]. Its wide application is limited due to its high cost and difficulty to regenerate[12]. Thus, research on the production of activated carbon from a renewable, low-cost indigenous agricultural waste has gained attention worldwide because of its low cost and highly abundant characteristics[13, 14]. Some of the agricultural wastes that have been studied as a possible source of activated carbon are wood[15], bagasse[16], coir pith[17] , orange peel[18] , coffee husk[19], pine cone[20], Date tree[21], sunflower seed hull[22], pine-fruit stones[23], hazelnut husks[24], rice hulls[25], oil palm stones[12], and Date husk[26]. This present article presents new data and the process of removal a real textile dyes has been

2 Experimental section

2.1 Chemicals and materials

Chitosan was purchased from India sea foods, Cochin, Kerala which is 92% deacetylated. Sodium tripolyphosphate (TPP) was purchased from Finar chemicals limited, (ahmedabad).Concentrated H_2SO_4 and HCL were purchased from Nice chemicals limited Cochin, Kerala. Glacial acetic acid was purchased from Sisco Research Laboratories private limited, Mumbai. Starch was purchased from CHEMSPURE Chennai. Glutaraldehyde was purchased from S D fine chemical Ltd (SDFCL) Mumbai.

2.2 Solution preparation

. For the preparation of stock solution, 0.5 g of methyl orange dye was weighed and dissolved in 1000 mL of deionised water to get 500 ppm/L (first stock solution). From this first stock solution take 100 mL methyl orange solution was drained and make up 1000 mL to get second stock solution of 50 ppm/L. The exact concentration of each methyl orange dye solution was calculated on mass basis and expressed in terms of mg L^{-1} of which the adsorption experiments were carried out using NCS/Starch binary blend was prepared in the absence and presence of crossing linking agent.

2.3 Batch adsorption experiments

The adsorption experiments were carried out through batch method by varying contact time, pH, initial concentration and adsorbent dose.

2.3.1 Effect of pH on the removal of Methyl orange dye

The pH is one of the most important parameter on adsorption of methyl orange dye from aqueous solutions, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the sorption of methyl orange dye solution, the batch equilibrium studies at different pH values were carried out in the range of 2 to 9, using 2N HCl and 2N NaOH solution. It was found that the highest uptake of methyl orange dye was obtained at optimum pH 8 and at this pH, the percent removal of methyl orange dye on Nanochitosan / starch binary blend without glu was 79% , Nanochitosan/ starch binary blend with glu was 82%.

Table 1 : Effect of pH on the removal of methyl orange dye

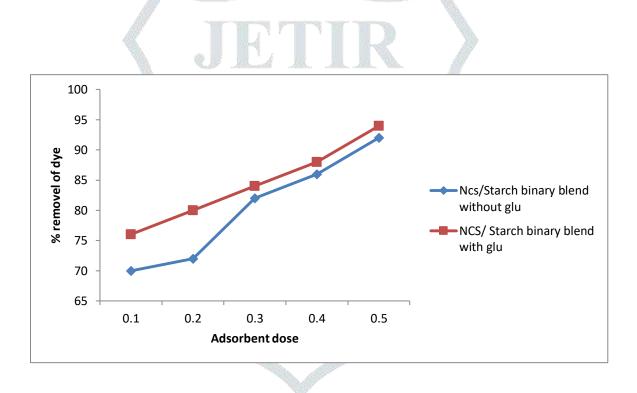| pH	% Removal of dye	
	NCS/Starch binary blend without glu	NCS/Starch binary blend with glu
2	36	35
3	40	44
4	52	58
5	58	65
6	65	68
7	74	75
8	79	82
9	75	79

Figure 1 : Effect of pH on the removel of methyl orange

Effect of adsorbent dose on the removal of methyl orange dye

Table 2: Effect of adsorbent dose on the removal of   methyl orange dye

Adsorbent dose (g)	% Removal of dye	
	NCS/Starch binary blend witouth glu	NCS/Starch binary blend with glu
0.1	70	76
0.2	72	80
0.3	82	84
0.4	86	88
0.5	92	94

Figure 2: Effect of adsorbent dose on the removel of methyl orange dye

The dependence on removel of methyl orange dye sorption on adsorbent dose was studied varying the amount of adsorbent dose from 0.1 to 0.5 g and keep the initial concentration (50 ppm /L), pH (2 to 9) and contact time (60 to 300 min) as constant. It was observed that maximum removal of methyl orange dye was obtained with 0.5 g adsorbent. This is due to the increased availability of active adsorption sites arising due to the increase effective surface area resulting from the increases in dose of adsorbent or due to conglomeration of the adsorbent. The number of available adsorption sites increases by increasing the sorbent and it results an increase in removal

efficiency. It can be concluded that by increasing the adsorbent dose, the removal efficiency increases (Alka Tiwari and Prerna Kathane, 2013).
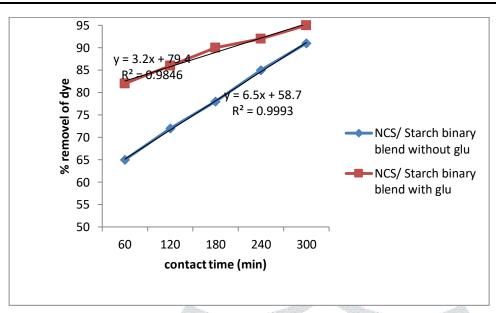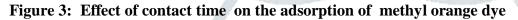
Effect of contact time on the removal of methyl orange dye

Table 3: Effect of contact time on the removal of methyl orange dye

Contact time (min)	% Removal of dye	
	NCS/Starch binary bkend without glu	NCS/ Starch binary blend with glu
60	65	82
120	72	86
180	78	90
240	85	92
300	92	96

The adsorption of heavy metal removel of methyl orange dye increased with increasing contact time and attains equilibrium after 300 min. From figure 3 the efficiency increases with increase in time of contact, due to the availability of more time for remove the heavy metal to make an attractive complex with the blend . It is important that, equilibrium time was one of the important parameters for an economical wastewater treatment system**.** Therefore the optimum time for maximum removal of methyl orange dye 91% in (NCS/ Starch binary blend without glu and 95% (NCS/Starch binary blend with glu was in 300 minutes. For the further optimization of other parameters, the contact time was considered as the equilibrium time corresponding to the adsorbent and adsorbate (Govindarajan et al., 2011).

Figure 3: Effect of contact time on the adsorption of methyl orange dye

Effect of initial concentration on the removal of methyl orange dye

The adsorbate and adsorbent interaction was studied by performing the adsorption experiments with different dye concentrations in the range of 500, 250, 200, 100 and 50 ppm. It was observed that with the increase in initial dye concentration, the percent removal of dye also decreases. This is due to the availability of less number of sites for the active adsorption on the surface of the composites.

Table 4: Effect of Initial Concentration on the removal of methyl orange dye

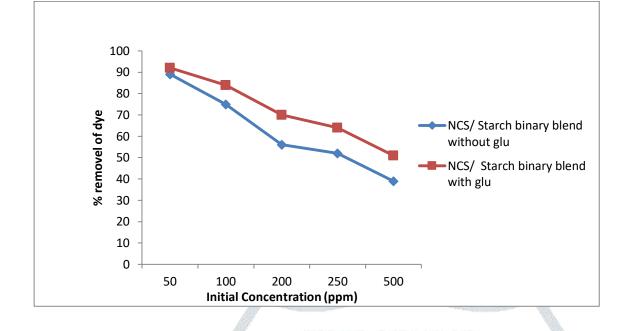| Initial concentration (ppm	% Removal of dye	
	NCS/Starch binary blend without glu	NCS/Starch binary blend with glu
50	89	92
100	75	84
200	56	70
250	52	64
500	39	51

Figure 4: Effect of Initial concentration on the adsorption of methyl orange dye

Kinetics studies

The kinetics removel of methyl orange biosorption on NCS/Starch binary blend without glu was analyzed using pseudo-first-order (Ho, 2004) and pseudo-second-order (Ho and Mckay, 1999) kinetics models.

Pseudo-first-order

The linearized form of pseudo-first-order Lagergren equation is given as Eq.

$$\log(qe - qt) = \log(qe) - \left(\frac{K_1}{2.303}\right) t$$

where q_e and q_t are the amounts of metal removel adsorbed (mg/g) at equilibrium and at time t (min), k_1 (min^{-1}) is the rate constant of pseudo-first- order adsorption rate, respectively. Linear plots of log (qe - qt) versus t was given in the figure 5
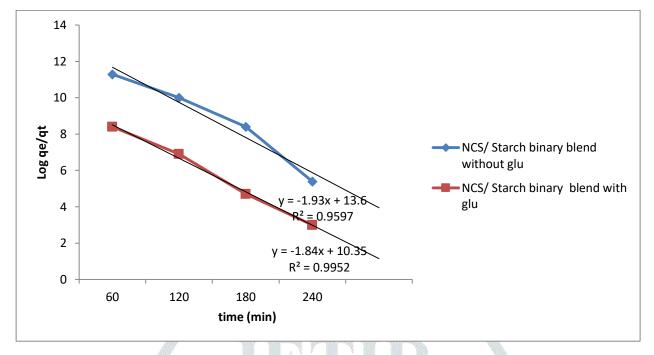
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Figure 5: Pseudo first order for methyl orange adsorption NCS/Starch binary blend without glu and with
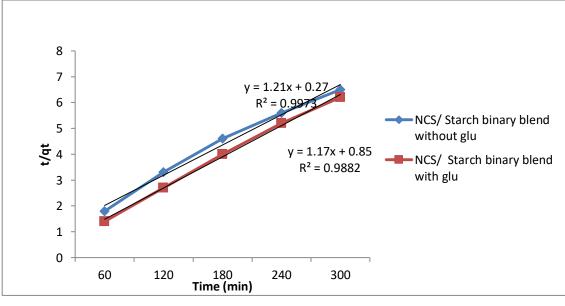
glu

Pseudo-Second-order

The pseudo-second-order rate equation is given as Eq. (Ho and Mckay, 1999)

$$t/q_t = 1/(k_2 q e^2) + t/q_e \qquad \text{----------------------(2)}$$

where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t (min) and k_2 (g mg^{-1} min^{-1}). With this equation, there is no problem in assigning an effective cue, because we and k_2 can be obtained from the slope and intercept of the plot of t/qt vs. t (Gerente et al., 2007), this is the adsorption rate constant of pseudo-second-order adsorption rate, respectively. The linear plots of (t/qt) versus t was given in the figure ------

Figure 6 : Pseudo second order for the removal of methyl orange NCS/Starch binary blend without and with glu

Table 5 : Comparison between Lagergren Pseudo- first-order and Pseudo- second order kinetic model for methyl orange on to NCS/Starch binary blend without and with glu

Adsorbent	Pseudo first order kinetic model			Experimental value	Pseudo- second-order kinetic model		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	q_e (mg/g)	k_2 (min^{-1})	R^2
NCS/Starch binary blend without glu	13.5	0.0759	0.946	46	52.63	0.00041	0.990
NCS/Starch binary blend with glu	10.45	0.0806	0.993	44.5	50	0.00125	0.999

The values of k_1 can be determined from the slope of the linear plot of log (qe−qt) versus t, and k_2 can be calculated from the slope of the linear plot t/qt versus t. The linear plots of two kinetic models are presented in Figure 5 and 6 respectively. The values of k_1, k_2, q_e and the correlation coefficient (R^2) from the linear plots are shown in Table 5. The pseudo-second-order linear plots resulted in higher R^2 values than the pseudo-first-order kinetic model. The values of q_e (Cal) from the pseudo-second-order was closer to q_e (exp) than that from the pseudo-first- order kinetics. These indicated the better applicability of the pseudo-second-order model. The pseudo-first-order linear plots resulted in lesser R^2 values than the pseudo-second-order.

Adsorption studies

The analysis of biosorption process requires a better understanding of the adsorption process. A dynamic equilibrium was established in the concentration of adsorbate between two phases. The equilibrium isotherm is of fundamental importance for the design and optimization of the adsorption system for the removal of heavy metal ions from the aqueous solution. The importance of these equilibrium studies was implemented in this present work described by use of Langmuir and Freundlich isotherm model.

Table 6: Distribution table for the adsorbent and the adsorbate NCS/Starch binary blend without glu

Initial concentration of dye in 50 ml	50	100	200	250	500
Equalent adsorption in 0.5 g of sorbent (qe)	46	84	140	160	255
Amount of dye left in solution	4	16	60	90	245
Ce/ye	0.0869	0.1905	0.4285	0.5625	0.9607

Table 7: Distribution table for the adsorbent and the adsorbate NCS/Starch binary blebd with glu

Initial concentration of dye in 50 ml	50	100	200	250	500
Equalent adsorption in 0.5 g of sorbent (qe)	44.5	75	112	130	185
Amount of dye left in solution	5.5	25	88	120	315
Ce/ye	0.1235	0.3333	0.7857	0.9230	1.702

Langmuir isotherm

The Langmuir equation describes monolayer adsorption. This model assumes a single layer of adsorbed solute at a constant temperature and a uniform energy of adsorption. The linear form of Langmuir isotherm may be represented as:

$$\frac{C_{eq}}{C_{ads}} = b\frac{C_{eq}}{K_L} + \frac{1}{K_L} \quad ------------- (3)$$

and $C_{max} = \dfrac{Kl}{b}$ --(4)

Where

C_{ads} = the amount of solute adsorbed per unit weight of adsorbent (mg/g),

C_{eq} = the equilibrium concentration of solute in the bulk solution (mg/dm^3),

C_{max} = the monolayer adsorption capacity (mg/g) and K_L is sorption equilibrium constant related to the free energy of adsorption

Figure 7: Langmuir isotherm for the removal of   methyl orange dye onto NCS/Starch binary blendwithoutglu

Figure 8: Langmuir isotherm for the removal of metal methyl orange onto NCS/Starch binary blend with glu

C_{max} represent a practical limiting adsorption capacity and when the surface is fully covered with heavy dye and assists in the comparison of adsorption performance, particularly in case where the sorbent did not reach

its full saturation in experiments. The values of q_{max} and K_a can be calculated from the slope and intercept of the plot of C_{eq}/C_{ads} versus C_{eq}. The values of K_L and C_{max} are given in Table 7.

To study the applicability of the Langmuir isotherm for adsorption on NCS/Starch binary blend with glu , a linear plot of C_e/q_e against C_e was plotted. The values of C_{max}, K_L and R^2 (coefficient of determination) are shown in Table 8.

Table 8: Adsorption isotherm constants constant, C_{max} and correlation coeficients NCS/Starch binary blend without and with glu removel of methyl orange dye

Adsorbent	$K_L(dm^3/g)$	$b(dm^3/g)$	$C_{max}(mg/g)$	R^2
NCS/Starch binary blend without glu	4.629	0.944	2.6315	0.920
NCS/Starch binary blend with glu	2.500	0.950	4.9020	0.930

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter ,R_L that is used to predict if an adsorption system is "favourable" or "unfavourable" (Ngah and Musa,1998).

The separation factor, R_L is definds by

$$R_L = \frac{1}{(1+bC_f}$$ ------------------------(5)

Where C_f is the final metal removel concentration (mg/ dm^3) and b is the Langmuir adsorption equilibrium constant (dm^3/mg). The parameter indicates the isotherm shape according to Table ----. The value of R_L calculated for different initial concentration of metal removel mg/L are given in the Table 1----. If the R_L values are in the range of metal removel onto nano composite of NCS/Starch binary blend removel of methyl orange dye is favorable.

Table 9 : Effect of separation facter on isotherm shape

R_L value	Type of isotherm
$R_{L>1}$	Unfavorable
$R_{L=1}$	Linear
$0 < R_{L<1}$	Favorable
$R_{L=0}$	Irreversible

Table 9 : R_L values based on Langmuir adsorption (NCS/Starch binary blend

Without and with glu removel of methyl orange dye

Adsorbent	Initial concentration mg/L	Final concentration mg/L	R_L value
NCS/starch binary blend without glu	50	4	0.6813
	100	16	0.3483
	200	60	0.1247
	250	90	0.0950
	500	245	0.0436
NCS/Starch binary blend with glu	50	5.5	0.1627
	100	25	0.7017
	200	86	0.4061
	250	120	0.3289
	500	315	0.1594

Where C_f is the final dye removel concentration (mg/dm^3) and *b* is the Langmuir adsorption equilibrium constant (dm^3/mg) the parameter indicates the isotherm shape according to Table ---. The separation factor ($R_L<1$) value for matel removel onto NCS/Starch binary blend without and with glu indicates that biosorption in this study was favorable.

Freundlich adsorption isotherm studies

The Freundlich equation is an empirical equation used to describe the distribution of solute between solid and aqueous phases at a point of saturation. This model assumes that there is an exponential variation in site energies of the adsorbent and also surface adsorption is not the rate limiting step. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. The Freundlich isotherm can be expressed by

$$q_e = K_f C_e^{1/n}$$ ---(6)

where K_F is the adsorption capacity at unit concentration (L/g) and $1/n$ is adsorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$). Eq. can be rearranged to a linear form:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$ ----------------------------------(7)

Where C_e is the equilibrium concentration (mg/dm3) and q_e is the amount adsorbed per unit mass of adsorbent (mg/g). When lnqe was plotted against ln C_e, a straight line was obtained, which shows a favorable adsorption of methylene blue dye following the Freundlich Isotherm. The values of K_f and n are given in Table-1------.

To study the applicability of the Freundlich for adsorption onto NCS /Starch binary blend with and without glu adsorbent, linear plot of log q_e versus log C_e was plotted. The values of K_F, n, and R^2 are shown in Table ---.

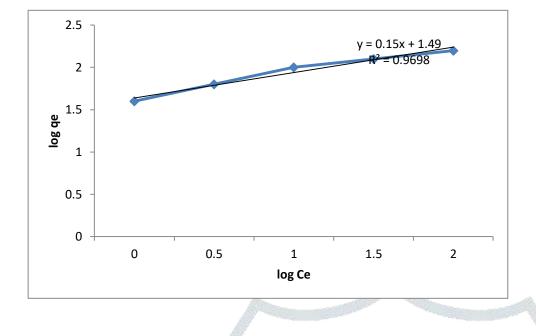**Figure 9 : Freundlich adsorption isotherm for the removel of methyl orange dye onto NCS/Starch binary**
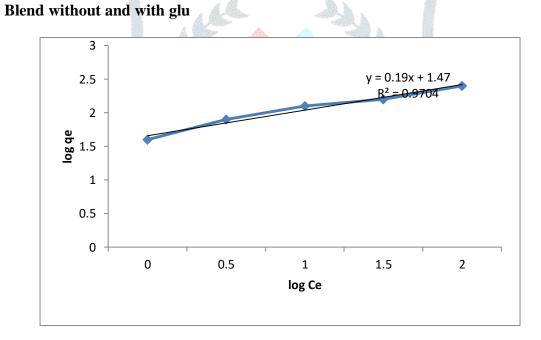
Blend without and with glu

Figure 9 : Freundlich adsorption isotherm for removal of methyl orange dye onto NCS/Starch binary

blend without and with glu

Table 10: Comparison between Langmuir isotherm and Freundlich isotherm for removel of methyl orange dye on to NCS/ Starch binary blend without and with glu

Adsorbent	Langmuir constants				Freundlich constants		
	K_L (dm³/g)	b (dm³/g)	C_{max} (mg/g)	R^2	K_F (dm³/g)	n(dm³/g)	R^2
NCS/Starch binary blend without glu	4.629	0.944	4.902	0.920	30.902	6.666	0.969
NCS/Starch binary blend with glu	2.500	0.950	2.631	0.930	29.512	5.263	0.970

Analysis of equilibrium data is important for developing an equation that can be used to design and optimize an operating procedure. To examine the relationship between biosorption and aqueous concentration at equilibrium, various biosorption isotherm models are widely employed for fitting the data. The Freundlich isotherm is originally empirical in nature (Freundlich, 1906), but was later interpreted as biosorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data (Aksu and Kutsal, 1991).

The value of *n*, of this model, falling in the range of 1– 10 indicates favourable biosorption (Aksu, 2002). The numerical value of 1/n < 1 indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by the adsorbate. Thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface (Hasany et al., 2002). The present study results indicate that the Freundlich model more R^2 value than Langmuir model. The adsorption data provided an excellent fit to the Freundlich isotherm. The separation factor (R_L) value indicates that methyl orange dye biosorption of biosorbent in this study is favourable. It can be seen from the table, NCS/Starch binary blend with glu used in this study has high biosorption capacity.

Conclusion

The adsorption experiment were carried out through batch method by varying contact time, pH, initial concentration, and adsorbent dose were calculated and the values are tabulated. Pseudo first order and second order kinetics are analysed. The R^2 value of pseudo first order NCS/Starch binary blend without and with glu removel of methyl orange dye are 0.995 and 0.959. So the present study results indicate that NCS/Starch binary blend without and with glu removel of methyl orange dye is fit the adsorption studies. In pseudo second order R^2 value NCS/Starch binary blend without and with glu removel of methyl orange are 0.988 and 0.997. NCS/Starch binary blend without and with glu removel of methyl orange is fit the metal removel adsorption studies.

In Langmuir constant NCS/Starch binary blend with glu removel of methyl orange dye is more R^2 value (0.930) compare to NCS/Starch binary blend without glu removel of methyl orange dye value (0.920). So NCS/ Starch binary blend with glu is fit the adsorption studies. In Freundlich constant NCS/Starch binary blend with glu removel of methyl orange is more R^2 value (0.970) compare to NCS/Starch binary blend without glu removel of methyl orange dye (0.969) So NCS/Starch binary blend with glu is fit the dye removel adsorption studies. The Freundlich model more R^2 value than Langmuir model. The adsorption data provided an excellent fit to the Freundlich isotherm.

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