

Full Length Research Paper

Removal of hazardous dye Ponceau-S by using chitin: An organic bioadsorbent

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There are numbers of applications of chitin for the removal of basic dyes and other colored organics from industrial effluents. In present research article there is focus on the preparation of bioadsorbent chitin and its application for the removal Ponceau-S dye from the aqueous solution by using chitin as an organic bioadsorbent. Chitin was characterized by scanning electron microscopy (SEM). Different parameters have been studied such as initial dye concentration, pH, contact time and adsorbent dose etc. In experimental study it is seen that the higher percent removal of Ponceau-S dye at optimum pH 3.5. Kinetics and equilibrium studies were also carried out by using the chitin which fit for Freundlich and Langmuir isotherm and kinetic study follows second order mechanism.

Key words: Chitin, Ponceau-S, organic bioadsorbent, colored organic, industrial effluents.

INTRODUCTION

Dye pollutants from textile dye industries are an important source of environment contamination. The dyes currently used in textile industry is about 10,000 (Poon et al., 1999). It is estimated that 1-155 of the dyes are lost during processes and is released in wastewater. The release of this colored wastewater poses a major problem for the industry as well as a threat to the environment (Sauer et al., 2002). Dye pollutants are generally resistant to biological degradation (Kuo and Ho 2001; Sun et al., 2002). The discharge of dyes in the environment is worrying for both toxicological and esthetical reason as dyes impede light penetration, damage the quality of the receiving streams and are toxic to food chain of organism (Padmesh et al., 2006). However, commercially available activated carbon is still considered expensive (Sourja et al., 2005). The world-wide high level of production and use of generates colored wastewater gives of environmental concern. Textile companies, dye manufacturing industries, paper had pulp mills, tanneries, electroplating factories, distilleries, food companies and a host other industries discharge colored wastewater (McKay et al., 1998).

Methods of color removal from industrial effluents include biological treatment, coagulation, flotation, adsorption, oxidation and higher filtration among the treatment options, adsorption appear to have considerable potential for the removal of color from industrial effluents. As the adsorption into active carbons is a well known process for micro pollutants removal (Faur-Brasquet et al., 2003). However, most of reactive dyes are non-degradable and toxic to environments and carcinogenic to human being. Even though it is treated with wastewater treatment, the solution contained reactive dyes with some color. Besides traditional physicochemical and biological treatment methods are effective to remove reactive dyes (Eoen and Acar, 2006; Ozcan et al., 2006; Akkaya et al., 2007; Gulnaz e al., 2006; Jain et al., 2003). It is reported that over 100,000 commercially available dyes exist and more than 7×10^5 metric tones of dyes are produces annually (Pearce et al., 2003; McMullan et al., 2001). Then widely used methods to treat dyes containing wastewaters are chemical precipitation, ion exchange, reverse osmosis, ozonation, solvent extraction, adsorption, membrane filtration and flocculation. Within these techniques, adsorption technology has been widely applied to treat dyes wastewater using various adsorbents such as activated carbon (AC), peat, sludge, algae, clay, Zeolite, flyash, and montmorillonite. Although AC is relatively expensive compared to other materials,

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it has been used as a common adsorbent because it has large surface area and high adsorption capacity to organics (Weng and Pan, 2006; Tunali et al., 2006). Recently, some crude lignocelluloses materials had been used as low cost adsorbent for removal of dyes from the aqueous solution, which included apple pomace wheat straw (Robinson et al., 2002). Corn cob and barley Robinson et al. (2002), kudzu Allen et al. (2003), rice husk Vadivelan and Kumar (2005), pine saw dust Ozacar and Sengil (2005), Peanut hull Gang et al. (2007), and kohlrabi Gang et al. (2005). Dyes are important materials that are currently in use both for domestic and industrial purposes. Since the invention of synthetic dyes in 1856, several forms of dyes are now available, and more than 8000 dyes are being manufactured and consequently used for specific purposes. The dyes in use are both water soluble and insoluble. The big consumers of dyes are textile, dyeing, paper and pulp, tannery, and paint industries. Hence, the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities for them to be considered an objectionable type of pollutant for two reasons: they impart color to water, which is not acceptable on aesthetic grounds, and they are toxic and adversely affect life (Nemerow and Doby, 1958; Walsh et al., 1980; Anthony, 1977).

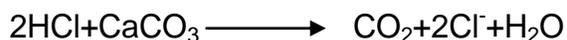
In various plants that are used for treating wastewater through adsorption, activated carbon is used as adsorbent. However, in view of the higher cost of activated carbons and difficulties associated with regeneration, attempts have been made by various workers to use low-cost natural materials or industrial wastes or by-products, collectively known as low-cost alternative adsorbents or low-cost adsorbents, or LCAs (low cost adsorbents). Some of the many LCAs that have been studied have proven to be effective and a number of them offer promise for the future (Gupta et al., 2009). Meticulous use of the waste materials and its management has been a challenge to mankind since long time and with the advancement of science man has always been in search of proper utility of waste materials. For the past two decades, adsorption technique has been well exploited to remove hazardous pollutants from the environment by employing waste materials. During this period of time, a large variety of waste materials particularly from industrial and agricultural waste products, which disposal has been a problem, have been successfully utilized for the removal of the toxic pollutants from the effluents disposed from the industry and household. Dyeing industries unknowingly dispose hazardous but precious dyes and have been the most benefited users of the discovery. By employing a suitable adsorbent they do not only save themselves from environmental authorities but also recovered their precious raw material successfully (Gupta et al., 2005). Among the consequences of this rapid growth is environmental disorder with huge pollution problem.

Besides other needs the demand for water ("Water for people water for Life" United Nations World Water Development Report (UNESCO) has increased tremendously with agricultural, industrial and domestic sectors consuming 70, 22 and 8% of the available fresh water, respectively and this has resulted in the generation of large amounts of wastewater, Helmer and Hespanhol, 1997, Nemerow, 1978 and Forgacs et al. (2004) containing a number of 'pollutants'. One of the important class of the pollutants is dyes, and once they enter the water it is no longer good and sometimes difficult to treat as the dyes have a synthetic origin and a complex molecular structure which makes them more stable and difficult to be biodegraded (Rai et al., 2005; Battacharya et al., 2003). The present paper is a thriving attempt to utilize low cost, easily available and prepared and no any sophisticated instrumentation required for the preparation of used adsorbent Chitin.

MATERIALS AND METHODS

Isolation of chitin from crab-shell

Dehooded crab-shell was collected, dried, crushed and decalcified by treatment with 10% HCl and the acid changes everyday. The dorsal cover of shell was peeled off on the third day. Its inner layer was removed rubbing it away with the fingers. Thereafter, the rest bone was broken into smaller bits. Therefore, the rest of the bone was completed in about four days which can be represented in following reaction.



The resulting chitin protein complex of the dorsal cover was deproteinized by treatment with distilled water at a 1:10 ratio and left for 24 h at room temperature for expanding. The expanded chitin was transferred into Buchner funnel and filtered off under vacuum. The weighed amount of chitin after expanding was washed with 6N HCl, rinsed with distilled water to reach filtered of neutral pH and filtered off under vacuum. Next 18% KOH solution was added to chitin which was then boiled for 3 h in water bath. After cooling, the chitin was rinsed with distilled water to reach neutral pH and filtered off under vacuum. The chitin had to be crushed to finer particles and finally prepared chitin was used for the further study.

Preparation of dye solution of different concentration

The stock solution of Ponceau-S dye of 10 to 100 mg/L is prepared. The stock solution used for the further study of adsorption. The Ponceau-S dye is the Azo-dye (HIMEDIA laboratories private limited) having molecular wt. 760.56 g was used. The structure Ponceau-S is shown in Figure 1.

Experimental methods and measurement

Experiments were carried out by using double beam spectrophotometer (Systronic)-2203 for the adsorption experiment on aqueous solution of Ponceau-S.

In every experimental stage an accurately weighed amount of chitin is added to the 100 ml red solution of Ponceau-S. The mixture was stirred on magnetic stirrer for different interval of time.

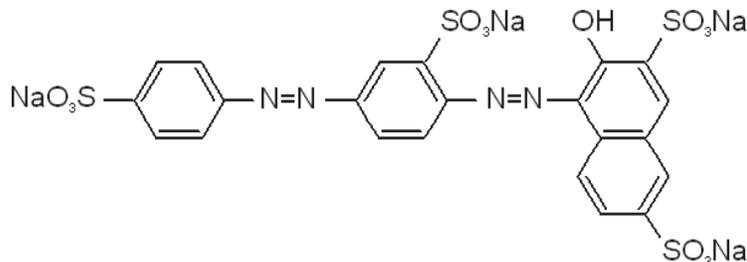


Figure 1. Structure of Ponceau-S.

After stirring of the solution, it was allowed to settle. Then absorbance of different concentrations was taken from Ponceau-S dye solution. Before and after treatment of adsorbent dosage on the double beam spectrophotometer at $\lambda_{max} = 519 \text{ nm}$ for Ponceau-S. The experiment was carried out at pH range from 1 to 12. The pH of the experimental solutions of different stages was maintained by 0.1N HCl and 0.1N NaOH (freshly prepared). Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution at different interval of time. Other parameters were studied such as initial dye concentration, adsorbent dosage, temperature and previously described parameter pH.

RESULTS AND DISCUSSION

Adsorbent characterization

For the identification of morphological, structural of chitin was carried out by SEM.

Scanning electron microscopy (SEM) analysis

The surface morphology of chitin before and after adsorption was visualized by scanning electron microscope (SEM) shown in Figures 2 and 3 respectively. The observation of SEM micrographs of the chitin showed rough areas of the surface and micropores were identifiable. Comparison of these micrographs before and after Ponceau-S sorption that the adsorption of Ponceau-S on the surface of the activated carbon.

Adsorption kinetics

In ordered to investigate the mechanism of sorption, several kinetics model were tested including pseudo first order model and pseudo second order model.

Pseudo first order model

Lagergrens rate equation is most widely used Ho and Mckay (1999) for the adsorption of adsorbate from solution. The first order Lagergrens rate equation is as follows;

$$\ln (q_e - q_t) = \ln q_e - k_1 t \dots\dots\dots (1)$$

Where q_e (mg/g) and q_t (mg/g) are the amount of Ponceau-S adsorbed at equilibrium and at time t , respectively, and k_1 is the first order rate constant (min^{-1}). The values of k_1 were calculated from plots of $\ln(q_e - q_t)$ Vs. t as shown in Figure 4 for different concentration of Ponceau-S. The experimental q_e values do not agree with the calculated ones obtained from linear plots (fig 4). This shows that adsorption of Ponceau-S into chitin is not a pseudo second order kinetics.

Pseudo second order model

Pseudo second order equation (Annadurai et al., 2002; Zhao et al., 1989) based on equilibrium adsorption is expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \dots\dots\dots (2)$$

Where k_2 (g/mg min) is the rate constant of second order adsorption. If second order is applicable, the plot of t/q_t Vs t should show a linear relationship. q_e and k_2 can be determine from the slope and intercept of the plot respectively. The linear plot of t/q_t Vs t as represented in Figure 5 show a good agreement between experimental q_e and calculated q_e values. The correlation coefficient for the second order kinetics model is greater than 0.98 and experimental q_e values agree with the calculated ones indicating the applicability of this kinetics equation. This can be determined from the Table 1. This shows that the adsorption process of Ponceau-S into chitin is a second order nature.

Effects of initial concentration of dyes

The effect of initial concentration of dye on the removal of Ponceau-S (In terms of percentage removal). The percentage removal of dye was found to be decreasing with the increase in initial dye concentration. This indicates that there exist reductions in immediate solute

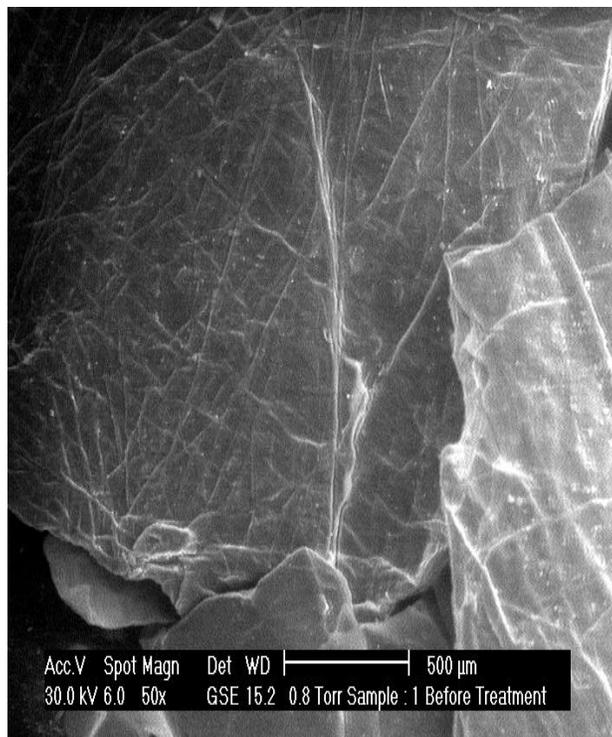


Figure 2. SEM analysis of chitin before adsorption of dye.



Figure 3. SEM analysis of chitin after adsorption of dye.

adsorption, owing to the lack of available active sites required for the high initial concentration of Ponceau-S.

The rate of percentage removal of Ponceau-S dye was studied by varying the dye concentration from 10 to 100

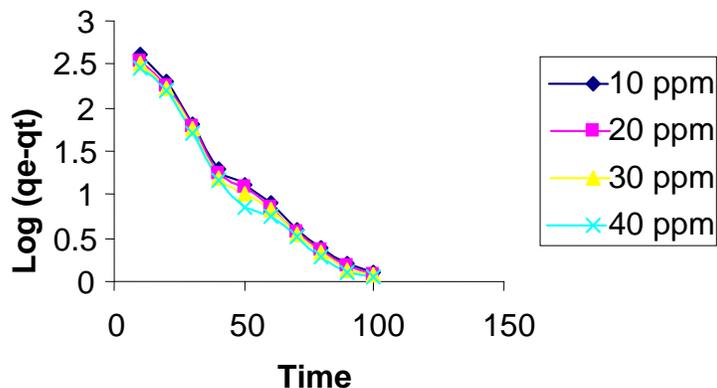


Figure 4. Pseudo first order kinetics of Ponceau-S adsorption on chitin.

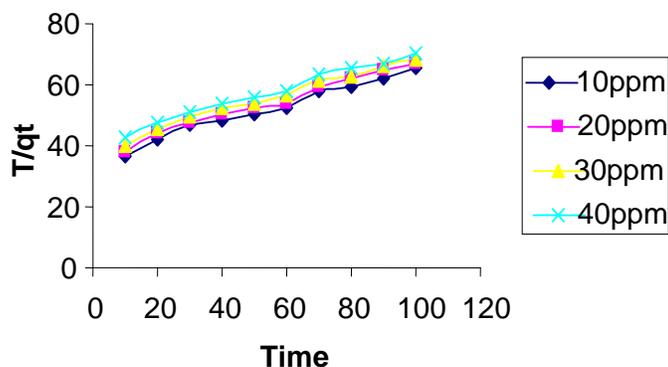


Figure 5. Pseudo second order kinetics for adsorption of Ponceau-S on chitin.

Table 1. Comparison of the pseudo first order and pseudo second order adsorption rate constants and calculated and experiments q_e values for different initial concentration.

Pseudo first order						
Adsorbent dose (g/L)	Initial concentration (mg/L)	q_e (exp.) (mg/g)	q_e (cal) (mg/g)	k_1 (min^{-1})	r^2	
3	30	3.89	0.078	3.87	0.964	
	50	3.85	0.059	3.78	0.961	
5	30	3.64	0.055	3.73	0.959	
	50	2.99	0.050	3.65	0.951	
Pseudo second order						
Adsorbent dose (g/L)	Initial concentration (mg/L)	q_e (cal) (mg/g)	k_2 ($\text{gmg}^{-1}\text{min}^{-1}$)	r^2		
3	30	0.033	3.	1		
	50	0.024	3.81	0.997		
5	30	0.020	3.75	0.998		
	50	0.018	3.69	.0999		

mg/L. The experiment was carried at fixed pH 8.4 and catalyst dose 50 mg/L. It was found that percentage

removal decreases from 100 to 10 mg/L as shown in Figure 6. Because for a fixed concentration of active sites

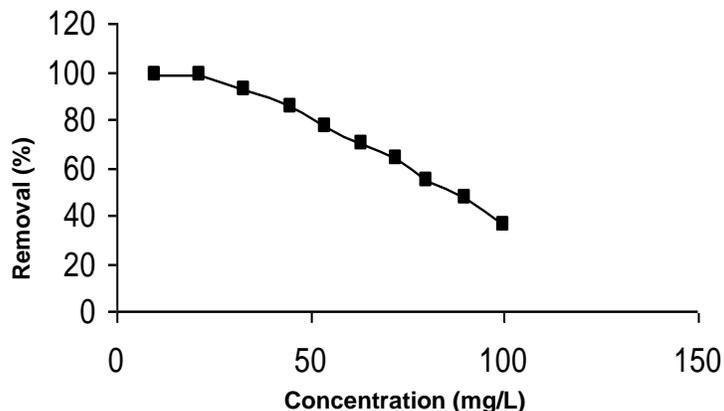


Figure 6. Effect of adsorbent concentration on dye removal at normal P^H with 5.0 g/L of adsorbent dose.

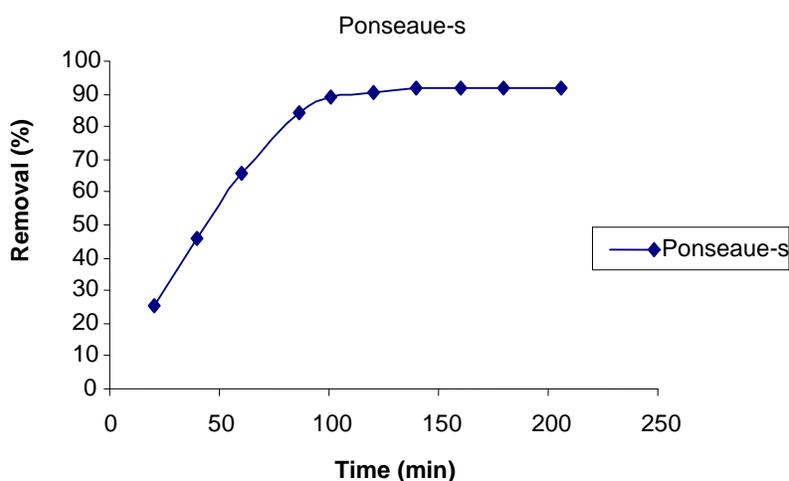


Figure 7. Effect of contact time on the removal Ponceau-S by chitin at normal P^H , adsorbent dose 0.5g/100 ml, 50 ppm concentration.

remaining the same, the number of substrates ions accommodated in the interlayer space increases so that the removed ones is decreased. This may be due to the fact that with increase in initial concentration of the dye, more dye molecules are also adsorbed on the surface of chitin.

Effect of contact time

The effect of contact time on the percentage removal of Ponceau-S was investigated at initial dye concentration from 10 to 50 mg/L as shown in Figure 7. The percentage removal of dye by chitin was fast at the beginning but it slowly decreased with time, it reached equilibrium which is the same for different concentration of ponceau-S. The optimum contact time of Ponceau-S removal was found to be 100 min. The rate of removal was higher in the

beginning due to the larger surface area available of adsorbent. After adsorption, rate of dye adsorbed is controlled due to the blocking surface area of adsorbent. After the equilibrium no adsorption takes place. The percent removal of dye Vs contact time is shown in the graph in Figure 7.

Effect of adsorbent dose

The effect of adsorbent dose in the percentage removal of Ponceau-S is shown in Figure 8. The percentage removal Ponceau-S increases with increase in dose of adsorbent. This is due to the increase availability of surface active sites resulting from the increase dose of adsorbent.

The effect of chitin dose on the removal ratio of dye is shown in Figure 8 along with the chitin dosage that

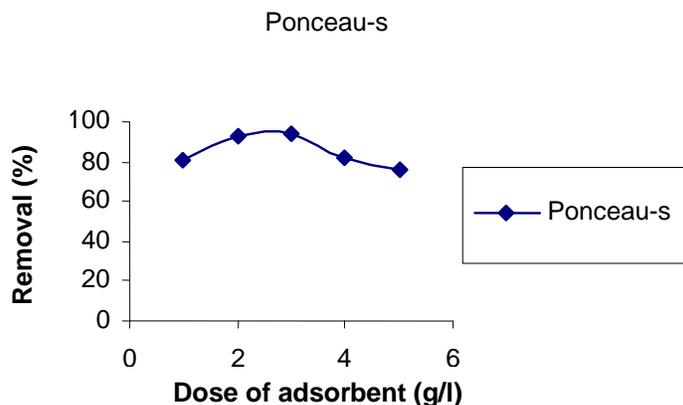


Figure 8. Effect of dose of adsorbent on the removal of dye at normal P^H and contact time=120 min and concentration of dye is 50 ppm.

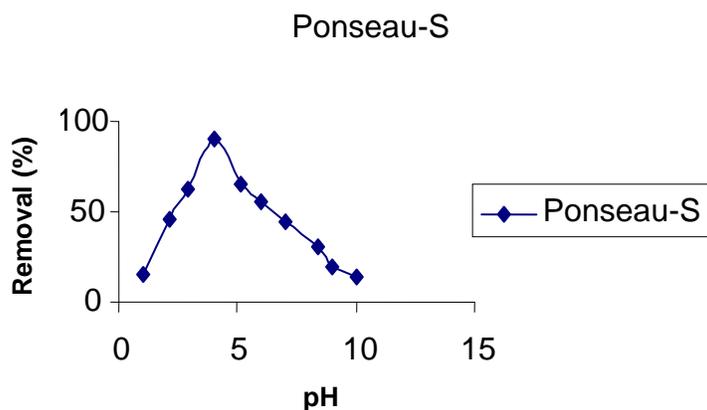


Figure 9. Effect of different pH on the removal of Ponceau-S from 50 mg/L dyes concentration, contact time 120 min. and adsorbent dose 5.0 g/L.

increased with 0.25 to 2g/L, the percentage of dye adsorbed increased from 20.0 to 95 percent in Ponceau-S. Above 2.0 g/L of chitin dose, the adsorption equilibrium of dye has been reached and the removal ratio of dyes held almost no variety. So the chitin dosage of 2.0 g/L was chosen for the subsequent experiments.

Effect of pH

One of the parameter studied in this present research is the pH. The effect of pH on removal of Ponceau-S and using 50 mg/L of dye and 5 g/100 ml of adsorbent dose was studied. The percent of removal or dye adsorption increased as initial pH was increased. The initial pH of the solution was reached at normal stage up to 6.5 to 7.5. Adsorption experiment was only conducted from 2 to 8 pH for Ponceau-S, dye removal ratio were minimum at

initial pH 2. The percent of dyes adsorbed increased as the initial pH increased. Beyond 3.5 pH, the maximum dye removal ratio was obtained and percentage of dye adsorbed kept basically unchangeable. For this reason, pH 3.5 of dyes solution was selected as the optimum P^H values for other experiments. This is shown in Figure 9.

Adsorption isotherm

Adsorption is time-dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing the dyes in wastewater. The relationship between initial dye concentration and adsorption percentage of dyes are shown in Figure 9. When the concentration were increased from 50 to 700 ppm. The percentage of adsorption Ponceau-S 96.34 to 80.45% and 97.54 to

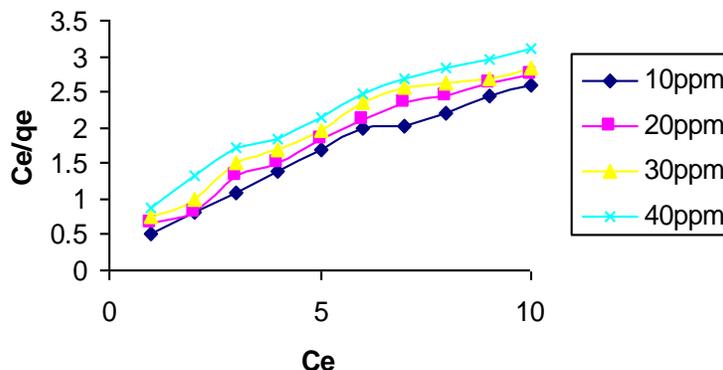


Figure 10. Langmuir isotherm for adsorption of Ponceau-s dye on chitin.

Table 2. Langmuir and Freundlich isotherm models constant and correlation coefficient for adsorption of Ponceau-S on prepared chitin.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	Qm(mg/g)	B(l/g)	r ²	K _f	1/n	r ²
chitin	3.3	0.499	0.993	5.205	0.28	0.982
	2.98	0.502	0.996	3.774	0.385	0.989
	2.90	0.508	0.991	2.01	0.499	0.99

65.35% respectively with the data in Figure 10. The Langmuir equation was employed to study the adsorption isotherm of Ponceau-S. The Langmuir equation is based on the assumption that maximum adsorption corresponds to saturate monolayer of the adsorbate molecule on the adsorbate surface, that the energy of adsorption is constant.

Langmuir isotherm

The Langmuir equation is shown as follows:

$$Ce/qe = 1 / (a \cdot Qm) + Ce/Qm \dots\dots\dots (3)$$

Where, Ce mg/L is the concentration of dye containing solution at equilibrium q_e be the amount dye adsorbed at equilibrium in mg/L. Q_m is the maximum adsorption and a is the Langmuir constant. Where, Q_m and a values are obtained from the slope (1/Q_m) and intercept (1/a.Q_m) of the linear plot of Ce/qe Vs Ce.

The Langmuir isotherm model is used to predict the sorption of aqueous compounds into a solid phase. This mechanistic model assumes that a monolayer of adsorbed material (in liquid, such as Ponceau-s) is adsorbed over a uniform adsorbent surface (a flat surface of solid phase, such as Chitin) at a constant temperature. The experimental data at equilibrium amount of adsorbed dye (eq) on the adsorbent (chitin) and the concentration in solution (eC) at a constant temperature and pH were used to describe the optimum isotherm model.

The straight lines Langmuir equation, the values of parameter and correlation coefficient of Langmuir equation of Ponceau-s adsorbed on chitin are given in Table 2. The experimental evidences show that the adsorption isotherm of Ponceau-S adsorbed on chitin is fit for Langmuir model. The (Q_m) maximum adsorption capacity of chitin for Ponceau-S was 298.32 mg/L. Whole data of maximum adsorption and Langmuir model is shown in Figure 10.

Freundlich isotherm

Equilibrium adsorption data of Ponceau-S dye on chitin was tested with Freundlich isotherm model. The linear plot of Freundlich isotherm at 303 K is employed to determine the intercept value of K_f and the slope 1/n along with R². Although, the value of R². (0.993) of Freundlich is slightly lower than the value of R². (0.999) of Langmuir isotherm. The value of 1/n (indicative of favorability) is 0.85, which is close to the unity and indicates the favorability of the adsorption process. Therefore, Freundlich model is still a good model to describe the adsorption data.

Conclusion

In the present article the chitin were prepared from the crustacean crab-shell which have been used successfully as an adsorbing agent for the removal of Ponceau-s dyes

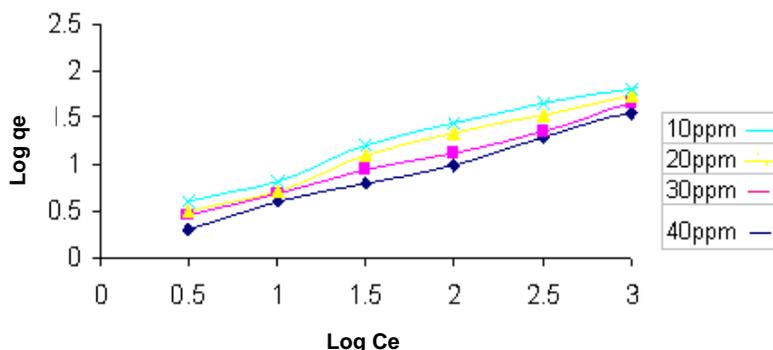


Figure 11. Freundlich isotherm for adsorption of Ponceau-S dye on chitin.

from the aqueous solutions. Adsorption was influenced by various parameters such as Initial P^H , Initial dye concentration, contact time and adsorbent dose. The maximum adsorption of Ponceau-S by chitin occurred at $pH=3.5$ for the Ponceau-S. Removal efficiency increased with decreasing dye concentration and increasing dose of adsorbent.

The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption equilibrium of Ponceau-S into chitin which is shown in Figure 11. The data were in good agreement with Langmuir and Freundlich isotherms. It was shown that the adsorption of Ponceau-S on to chitin best fitted by pseudo first order and pseudo second order kinetics. The adsorbent were characterized by SEM to detect adsorption capacity of the chitin. Since chitin were available in many crustaceans like cockroach, prawn and crabs etc. and also available in the market, the adsorption process is very important responsible for the textile industrial wastewater treatment.

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