International Journal of Waste Resources
ISSN: 2252-5211
Rahman and Akter, Int J Waste Resour 2016, 6:3
DOI: 10.4172/2252-5211.1000244
Research Article Open Access

Removal of Dyes Form Textile Wastewater by Adsorption using Shrimp Shell

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Abstract

Dye removal from textile wastewater has been a big challenge over the last decades. The effectiveness of adsorption for dyes removal from wastewater has made it an ideal alternative to other expensive treatment methods. This study inspects the possible use of chitin for the removal of dye from textile wastewater. Chitin was prepared from shrimp shell by a chemical process involving demineralization, de proteinization and decolorization. Prepared chitin was characterized by FTIR spectral analysis. The effects of various conditions such as adsorbent dose, pH and contact time were studied for this work. By using 1.5 g of chitin for 25 mL solution, the removal efficiency was achieved almost 96% at p^H = 5 where the retention time was 60 minutes. The adsorbent behavior was studied on the basis of Langmuir isotherm model. The equilibrium adsorption data were fitted to the Langmuir isotherm equation. This study provides a cost effective and environment friendly dye removal process for textile wastewater treatment.

Keywords: Shrimp shell; Chitin; Wastewater; Dye removal efficiency; Biological Oxygen Demand (BOD); Chemical Oxygen Demand (COD); Fourier Transform Infrared Spectroscopy (FT-IR)

Introduction

Textile knit industry uses large amount of organic and inorganic chemicals as dyes that are directly or indirectly responsible for producing wastewater. The rate of wastewater disposals from the textile industries is reaching a warning level nowadays.

The discarding of colored wastes into the water bodies damages the environment and toxic to human and aquatic life. The wastewater contains very high concentration of COD and BOD; and huge amount of suspended solids and other contaminants. Most sophisticated methods are required for treating wastewater in textile industries. Methods such as chemical, coagulation, flocculation, reverse osmosis, Nano-filtration, Ultra-filtration have been recommended. However these methods are very much complex and expensive. That is why these methods are not affordable to textiles industries in developing countries like Bangladesh.

Adsorption has gained supreme importance for environment protection by removing textile dyes from disposed water. Some of the adsorbents are effective in removing dyes and various pollutants, but some are not. That is why, new effective adsorbents are needed which should be cost effective, energy efficient, design flexible, biodegradable and available.

At present year different cost effective, commercially available adsorbents have been used for the removal of dyes from textile wastewater. However, the adsorption capacities of all the above adsorbents that are low cost and biodegradable are highly demanded. Chitin is a natural carbohydrate polymer found partially in the shells of crustaceans such as crab, shrimp, the cuticles of insects and the cells of fungi [1]. In Bangladesh shrimp are found from the coastal region of Satkhira, Khulna, Bagerhat and Cox's bazaar district. Chitin is considered as high efficient bio-adsorbent due to a high number of functional groups: N-acetyl amine, amine and hydroxyl [1-3]. The chitin was prepared from shrimp shell that was used to carry out this research. The aim of this study was to exploit the potential of the prepared chitin as a bio - adsorbent for removing reactive dyes from textile wastewater with respect to amount of adsorbents, pH values, and contact time and applied Langmuir adsorption isotherm model to verify this study [4-10].

Materials and Methods

Structure of chitin

Chitin $(C_8H_{13}O_5N)_n$ is a long -chain organic polymer of a N- acetyl glucosamine that is a derivative of glucose. In terms of structure, chitin may be related to the polysaccharide cellulose and, in terms of role, to the protein keratin.

Sample and adsorbents collection

In this experiment, wastewater sample was collected from Sharp Knitting & Dyeing Limited, Pagar, Tongi, Bangladesh. The sample contains mainly three types of reactive dyes as Deazol Black B EAN, Deafix Red ME 6BL and Firstfix Yellow 3RS. Chitin was used as an adsorbent for treating this wastewater. Chitin was prepared from shrimp shell that was collected from local fish market.

Preparation of adsorbents

The shrimp shells were washed with distilled water to remove dust and soluble impurities. After that the shrimp shells were dried in sun for longer period until completely dried. To obtain a uniform size product, the dried shells were ground through a centrifugal mortar. Then the shells were demineralized with 5% hydrochloric acid at ambient temperature with a solid to solvent ration of 1:14 (w/v) for 24 hours. The Demineralized shells were deproteinized with 5% NaOH solution for 24 hours at 400°C temperature with solid to solvent ratio 1:14 (w/v). Samples were then washed with distilled water & decolorized with acetone. The samples were dried until the powder was crispy. The Resultant product was chitin [11-14].

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Received August 06, 2016; **Accepted** August 08, 2016; **Published** August 15, 2016

Citation: Rahman FBA, Akter M (2016) Removal of Dyes Form Textile Wastewater by Adsorption using Shrimp Shell. Int J Waste Resour 6: 244. doi: 10.4172/2252-5211.1000244

Preparation of standard solution

1 L of stock solution of Deazol Black B EAN reactive dye was prepared by dissolving a mixture of 0.1 g of dye in a volumetric flask followed by dilution up to the mark addition of de-ionized water. Prepared standard solution was used for the study of adsorption isotherm.

Procedures

Batch adsorption experiment was conducted by stirring a series of glass bottles containing 25 mL sample wastewater with different adsorbent amount (0.5, 1.0,1.5, 2.0 and 2.5 g) for different time intervals (30, 60, 90,120 minutes) at room temperature. The help of magnetic stirrer did the stirring. The stirring proceeded for 2 hours until the equilibrium reached. After which the mixture was left to settle for 3 hours. Then the solution was filtered with the help of filter paper. The filtrate's absorbance was determined by using US-VIS spectrometer at adjusted λ_{max}. The followed adsorption experiment carried out.

Experiment 1: The effect of contact time: In this eperiment various effects of contact time between adsorbate and adsorbent were studied. The range of contact time was 30 to 120 minutes at p^H=7 and 2 g of adsorbent used for making 25 mL solution.

Experiment 2: The Effect of p^H: 25 mL of solution was made using 1.5 g of adsorbent. The optimum contact time between adsorbate and adsorbent was 90 minutes. The pH was varied from 5 to 9. p^H was adjusted using acetic acid and NaOH.

Experiment 3: The effect of amount of adsorbent: This experiment was the observation of effects of adsorbent amount in waste removal. The range of adsorbent amount was 0.5 g to 2 g for 25 mL of solution. The optimum time for contact was 90 minutes at p^H value 7.

Experiment 4: Adsorption Isotherm for pure reactive dye onto shrimp shell: This experiment studied Langmuir adsorption isotherm onto the chitin of shrimp shell. A suitable condition was set that found from previous experiments to carry out this experiment.

Results and Discussion

Effects of amount of adsorbent

Figure 1 shows the percentage removal of waste from textile wastewater sample at p^H=7 for adsorbent dosage from 0.5 g to 2.5 g. This experiment was carried out at room temperature and the contact time was 90 minutes. The result explained that the waste removal percentage was very low at beginning. Then percentage increased with increasing amount of dosage. This happened because initially the active site of adsorbent could not effectively contact with adsorbate. When the adsorbent amount was higher, the active portion was available for removing almost all the waste from sample wastewater. And the figure shows that the optimum amount of dose of chitin is 2 g at which maximum amount of dyes were removed. The maximum removal percentage is almost 96-97%. Above 2 g of chitin dose, the proper contact did not happened, so the removal percentage decreased [15-20].

Effects of dye-adsorbent contact time

The dye removal percentage from sample wastewater with contact time between adsorbate and adsorbent is shown in Figure 2. The range of observed contact time was 30-120 minutes with the increment of 30 minutes. The experiment was carried out for optimum adsorbent dosage of 2 g at room temperature. The optimum p^H of sample wastewater was 7. The result revealed that the rate of dye removal

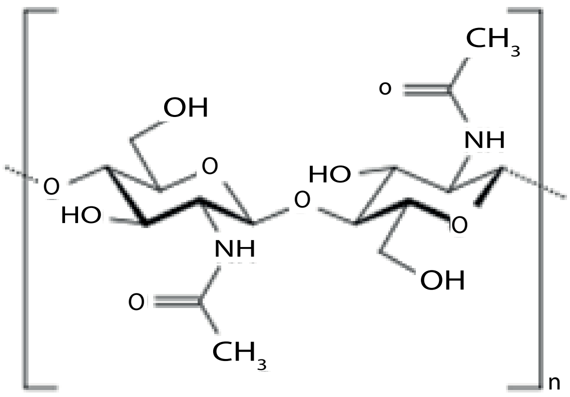

Figure 1: Structure of shrimp shell chitin.

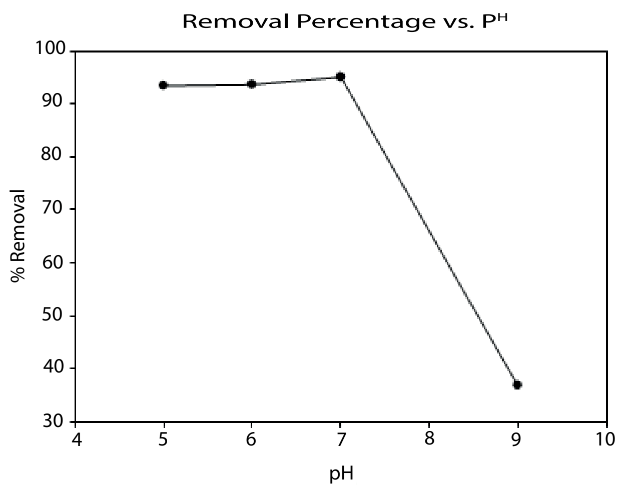

Figure 2: Effect of shrimp shell chitin dosage on the removal of dyes by adsorption onto shrimp shell. (Initial concentration: 1.5 g/25 mL; pH value: 7; and contact time: 90 minutes).

percentage was very at the beginning of the experiment due to improper contact of adsorbent with dye in wastewater. Further, as contact time increased, the dye removal percentage also increased. For contact time 60 minutes the removal percentage was found maximum and the value was almost 95%. But after 60 minutes contact time the removal percentage was decreased with time increased [21,22].

Effects of p^H

The pH value of the solution is an important parameter for the adsorption processes, and the initial pH value of the solution has significant influence compared to than the final p^H. To study the effect of p^H on dyes adsorption, the experiment was carried out at 1.5 g/25 mL at room temperature. In general, the initial p^H value may enhance or depress the uptake. This is attributed to the change of adsorbent surface with the change of p^H value. Figure 3 shows the relationship between p^H values and percentage removal of dyes from wastewater sample. The value of p^H varied from 5 to 9. The optimum dose amount was 2 g and contact time was 60 minutes. The result revealed that the rate of percent removal of dyes from wastewater sample was 93% at beginning. Further, the increasing the value of p^H of sample the removal percentage also

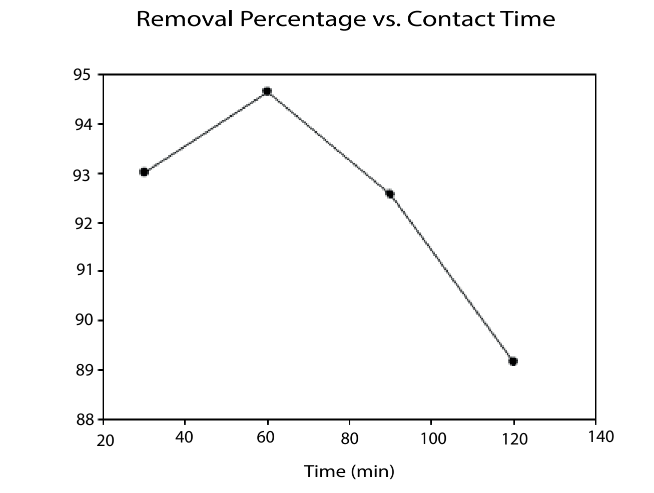

Figure 3: Effect of contact time on the removal of dyes by adsorption onto shrimp shell chitin. Initial concentration: 6 g/mL, Amount of chitin peel: 1.5 g and pH value: 7.

increased very slightly. However, for p^H above 7 the removal percentage was decreased very rapidly for improper contact of adsorbent [23-26].

Adsorption

The purpose of the adsorption isotherms is to relate the adsorbent concentration in the bulk solution and the adsorbed amount at the interface. The equilibrium isotherms in this study have been described in terms of Langmuir isotherm model. This adsorption model was plotted to study the removal capacity of materials. The Langmuir isotherm is an empirical equation assuming that the adsorption process take places as homogeneous sites, all sites are equivalent and there are no interactions between adsorbate molecule and adjacent sites. The adsorption data were analyzed according to the linear form of the Langmuir isotherm equation. A linear form of the Langmuir Isotherm equation is generally expressed as follows, Where C_e represents the equilibrium dye concentration in solution (mg/L), qe is the adsorption capacities (amount of dye adsorbed per weight of adsorbent, (mg/g) q_m and K_a are Langmuir constant that can be determined from above Langmuir linear equitation. This adsorption experiment was carried out for only Deazol Black B EAN reactive dyes. The absorbance of the clear solution was measured spectrophotometrically at maximum wavelength 601 nm.

Figure 4 also showed that adsorption of the Deazol Black B EAN dye fits well to angmuir isotherm model with the correlation coefficient (R2) of 0.997, supporting monolayer converge of the adsorbate on the surface of the adsorbent. The results found from Langmuir isotherm model are illustrated by Table 1.

The plot of $1/q_e$ versus $1/C_e$ showed that adsorption follow Langmuir isotherm model as illustrated in Figure 5. This figure employed to evaluate the value of q_m and K_a from the slope and intersect of the plot that presented in Table 1.

Characterization of prepared chitin by FTIR spectroscopy

The FT-IR spectrum of chitin prepared from shrimp shells is showed in Figure 6. The FT-IR spectrum presented a broad adsorption bond at around 3451 cm^{-1} corresponding to the vibrational stretching of hydrogen bonded N-H and O-H. The spectrum also shared characteristics peaks of amide I at 1657 cm^{-1} (C = O stretching), amide

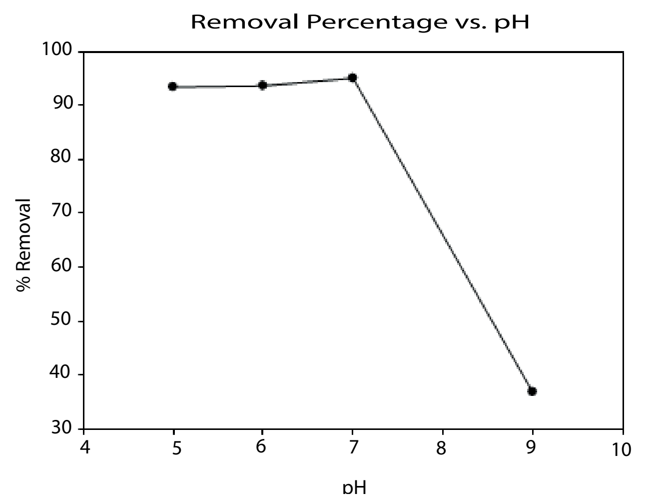

Figure 4: Effect of pH on the removal of dyes by adsorption onto shrimp shell chitin. Initial concentration: 6 g/L, amount of adsorbent: 1.5 g and contact time: 90 minutes.

Adsorbent	Dye	Langmuirisotherm equation		
		R^2	qm (mg/L)	Ka
Banana peel	Deazol Black B EAN	0.997	3.583	0.939

Table 1: Parameters obtained from correlation of Langmuir adsorption isotherm.

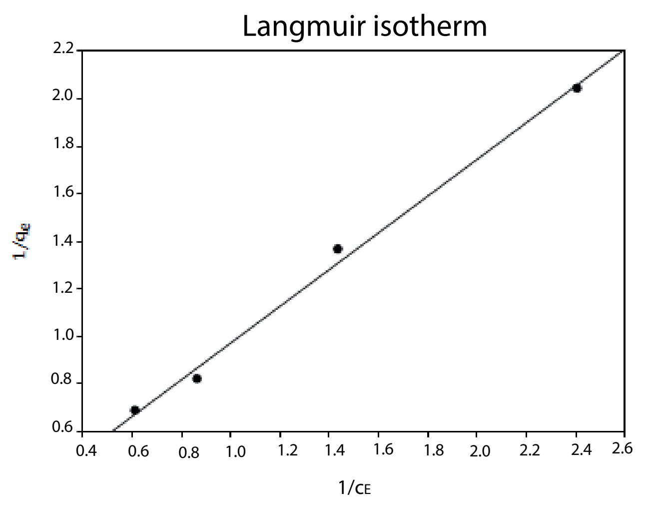

Figure 5: Langmuir isotherm for Deazol Black B EAN reactive dye onto banana peel (initial concentration: 20--60 mg/L; time: 180 minutes, pH: 6.5--7; room temperature).

II at 1566 cm^{-1} (N-H in plane deformation coupled with O-H in the plane deformation) and CH_2 wagging coupled with O-H in the plane deformation at 1322 cm^{-1}. The peaks observed at around 2932 and 2891 cm were assigned to sp3 C-H stretching (symmetric and asymmetric). The band at 1381 cm^{-1} corresponded to C-H bending and symmetric CH_3 deformation, while the bond at 1426 cm^{-1} was due to CH_2 bending and CH_3 deformation. The bend observed at 1160 cm -1 was indicated

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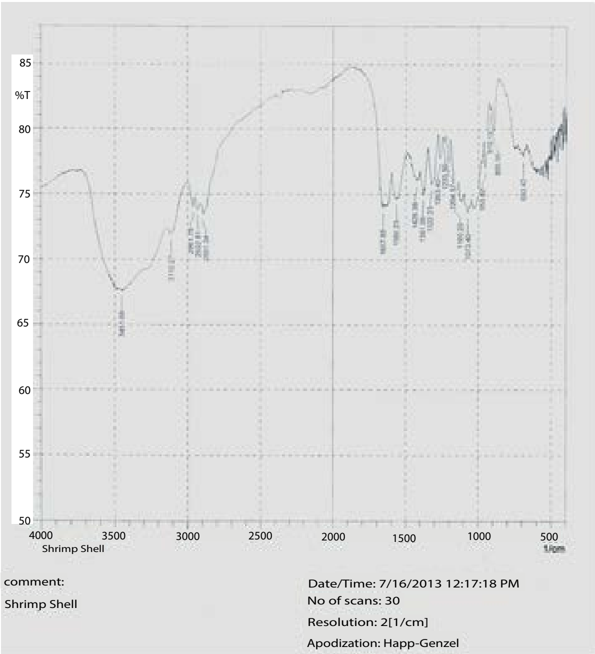

Figure 6: FT-IR spectrum for prepared chitin.

a bridged oxygen stretching (C-O-C linkage of ring). The C = O Stretching vibration bonds were observed at 1073 and 953 cm^{-1}. The characteristics peak for CH deformation of the β -glycosidic bond was observed at 896 cm^{-1}.

Conclusion

In this work the removal of reactive dyes from textile wastewater by batch adsorption using shrimp shell (chitin) was investigated. This study monitored the ability of chitin for removing dyes from wastewater with various adsorbent dose, contact time and p^H. The maximum percentage of dyes reduction was obtained at an optimum dose of 2 g, an optimum contact time of 60 minutes and an optimum p^H of 7. Shrimp shell chitin has been found to be comparatively better adsorbent because it can remove almost 96-97% of dyes from the wastewater. Finally, the result of adsorption study, it is concluded that shrimp shell chitin can be used as a coagulant for reactive dyes from textile wastewater because of its higher adsorptive capacity, cost effectiveness, environment friendly behavior and availability in nature [27-30].

Acknowledgement

At first, we hereby express our utmost gratitude to the almighty Allah for successful completion of this research. I am deeply indebted to my honorable supervisor Dr. M. Zainal Abedin, Professor, Department of environment management, Independent University, Bangladesh who provided his encouraging guidance, thoughtful suggestion which were essential ingredients to complete this work. It was his constructive comments which made me able to bring this work to a successful completion. I also wish to thank all the faculty members for their help during the project.

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