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Research article

Removal of a textile dye using bioadsorbent chitin obtained from harmful insect, *Polyphylla fullo* (Coleoptera: Scarabaeidae)

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Abstract: The novel bioadsorbent, *Polyphylla fullo* chitin, was utilized for Lanaset Blue-2R removal from aqueous solution. The characterization of *P. fullo* chitin was investigated by FT-IR and SEM techniques. Dye removal studies were carried out in a batch system. Removal performance of the bioadsorbent was evaluated under various conditions: bioadsorbent amount, solution pH, contact time, interfering ions and initial dye concentration. SEM micrographs revealed that the highly porous surface of *P. fullo* chitin could act as promising material for the removal of Lanaset Blue-2R dye. The effect of solution pH on the removal of dye was significant. Maximum dye removal value was obtained at pH 5. The presented study proofs that a novel and low cost material, *P. fullo* chitin, can be utilized as an effective biosorbent (above 90 %) for removal of a textile dye from aqueous solutions.

Keywords: *Polyphylla fullo*, chitin, lanaset Blue 2, UV-Vis. spectroscopy.

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Introduction

Water is the most essential material to all living organisms. Organic dyes are generally used as a colorant product in textiles, dyestuffs, and plastics, which leads to huge amounts of colored wastewater discharge to the environment (Li et al., 2018). These industrial wastewaters contain different kinds of substances some of them are accepted as organic and inorganic toxic pollutants. The most known of these materials are heavy metal ions and water soluble synthetic dyes. The environmental pollution and destruction resulted by these materials has raised rapidly and become an environmental threat for sustainable development (Tao et al., 2016).

Because of the complex chemical structure of synthetic dyes most of these molecules are non-biodegradable and remains stable in aquatic media. Furthermore, some of these organic dyes are genotoxic, mutagenic even carcinogenic, and may cause serious threats to human health as well as other living organisms (Song et al., 2017; Naderi et al., 2018). As a consequence, the treatment of dye contaminated wastewaters by using efficient methods is of prime scientific interest (Feng et al., 2013).

There are various methods for the treatment of synthetic dye containing wastewaters from aqueous solutions. The most known of these methods are membrane filtration, adsorption, coagulation, flocculation, enzymatic decomposition and oxidation (Feng et al., 2017).

The removal of toxic dye molecules by adsorption method is one of the most promising methods because it is easy to operate, effective, and relatively low cost. There are various types of adsorbents such as synthetic resins, clays, biomaterials, activated carbon and derivatives, that have used to remove dye molecules from aqueous solutions (Tao et al., 2016).

The biomass originated adsorbents (biomaterials) obtained from biological organisms (bio-adsorbents) have attracted considerable amount of interest in recent years. These bio-adsorbents can be considered as efficient adsorbents because they contain reactive groups such as amino, amido, acetamido, carbonyl, and sulphydryl etc. to

form metal chelates or complexes (Renu et al., 2017; Safinejad et al., 2017). These phenomena can be described as biosorption which is defined as a process of adsorption performed on the surfaces of dead or living biomass (Azin & Moghimi, 2018).

Chitin is a biocompatible, biodegradable and the second most abundant natural biopolymer in the world. This biopolymer has a rigid crystalline chemical structure and it is also stable in most common organic and inorganic solvents (Ghourbapour et al., 2019). The chemical structure of chitin is composed of *N*-acetyl-d-glucosamine residues, attached by β-(1,4) glycosidic linkage. every chitin chain is associated with neighbor one by hydrogen bond, where amino group of the molecule bonds with carbonyl group of the adjacent one (Komi and Hamblin, 2016). These amino and carbonyl groups of chitin allow its possible use as an alternative adsorbent.

Polyphylla fullo is found in North Africa and Europe. It is one of the most damaging pests of young orchards and vineyards, potatoes and many other crops in southwestern Turkey. The C-shaped larvae is called white grubs, live in the soil. They generally are creamy white with three pairs of legs and attack the root system of many crops. Young larvae feed on humus and the roots of herbaceous plants; older larvae gnaw through the roots of shrubs and trees, and severe feeding injuries result in wilting and often death of infested plants (Erler & Ateş, 2015).

The aim of this study is to isolate the specific chitin from *P. fullo* (a common pest that gives significant damages to many kind of crops) and investigate the biosorbent characteristics of this isolated chitin for a textile dye Lanaset Blue 2R from aqueous solutions.

Materials and Method

Chemicals

Polyphylla fullo pest samples were collected from Nigde, Turkey. Obtained pure chitin powder (100-250 mesh) was prepared from the collected *P. fullo* pests. Doubly distilled water was used for preparation of all aqueous solutions in the experiments. Stock dye solutions were prepared from solid powder of Lanaset Blue 2R (LB2R) obtained from a textile factory in Niğde. All other chemicals and reagents were purchased from Sigma-Aldrich (USA). H_3PO_4 and Na_2HPO_4 for pH 2-3, CH_3COOH and CH_3COONa for pH 4-5, Na_2HPO_4 and NaH_2PO_4 for pH 6-8 were used for preparation of buffer solutions with 0.25 mol L^{-1} of ionic strength.

Instruments

A Shimadzu UV-160A (Shimadzu, Japan) ultraviolet-visible spectrometer was used to measure the absorbance of LB2R solutions. A Hanna 2211 model digital pH-meter (Hanna, USA) was used for pH measurements of the aqueous and buffer solutions.

Preparation of biosorbent Polyphylla fullo chitin powder

Chitin powders were isolated from *P. fullo*. The isolation procedure was conventional acid and base treatment method. Firstly, the oven dried *P. fullo* samples were mechanically grinded in a mortar. The powdered samples were mixed with distilled water at a ratio of 1/10(w/v) at 75 °C for 5 h. After filtering the samples was dried and sieved with a 100-mesh sieve. A 5 g of the scaled samples was treated with1 M HCl for 12 h at room temperature. The residues were filtered and washed with doubly distilled water. Then the residues were treated with 1M NaOH for 3 h at 75 °C to remove proteins. Finally, the mixtures were decoloured with ethyl alcohol for 5 h at 75 °C. The resultants were washed and dried. *Polyphylla fullo* chitin products were available after passing through a 100-mesh sieve.

Solid-phase extraction procedure

100 mg of chitin was weighed and slurred in water. This suspension was transferred into the 100 mL pyrex beaker. 95 mL of aqueous solution, containing 100 μg of LB2R dye was adjusted to pH 6 by adding 5 mL of buffer solution. The 100 mL final solution (100 ppm LB2R) was transferred in to the pyrex beaker. The bioadsorbent–dye mixture was stirred at 300 rpm for 60 minutes. After the equilibrium, the solution was filtered and the final concentration of the LB2R was measured by UV-Visible spectrophotometer. The dye removal percentage was calculated by following formula.

$$CR(\%) = \frac{A_0 - A_t}{A_0} x100$$

where A_0 and A_t are the initial and final absorbances of LB2R respectively and CR (%) colour removal percentage of bioadsorbent. Effect of pH on the removal efficiency was investigated in a range of 2–8 at 100 mL dye solution (dye concentration: 100 mg/L) with 0.1 g adsorbent for 1 h. The effect of biosorbent quantity on the removal efficiency was investigated from 0.1 g 2 g in 100 mL dye solution. Effect of initial dye concentration on the colour removal was investigated in a concentration range from 10 to 250 mg/L with a biosorbent quantity of 0.5 g at pH 6.

All of the experiments were achieved at room temperature in triplicate.

Real sample preparation

The wastewater samples were collected from a textile factory in Niğde, Turkey. Samples were collected in plastic polyethylene bottles. The water samples were kept in dark at 4 °C until analysis. The optimized procedure was applied directly and analyte adding to wastewater for removal of LB2R content after pH adjustments.

Results and Discussion

The UV-Visible Spectrum of LB2R Dye

The UV-Vis. spectrum and the chemical structure of the Lanaset Blue-2R the substance to be removed from the aqueous medium is shown in Figure 1.

According to Uv/Vis. spectrum in Figure 1 there are two maximum absorbance peaks at 586 and 630 nm. Both of them could be used for determination of analyte concentration and 630 nm was chosen throughout the experiments.

Effect of pH

The solution pH is one of the most important parameters that affect the adsorption phenomena. This can occur both on the surface charge of the chitin and also in the ionization of the dye molecules. In this study, the effect of solution pH was investigated between pH 2 to pH 8 and the obtained results are given in Figure 2. In the figure there can be seen two region peaked at pH 5. Until and after pH 5 (CR value 95%) the removal of LB2R decreased. So, the pH 5.0 value was selected as optimum pH and used for further experiments.

The mechanism for the removal of LB2R can be explain by two possible interactions. Firstly, the chitin has capability to adsorb contaminants because of its amino groups in the chemical structure and its Lewis base character. As a result, positively charged chitin and negatively charged dye molecules create an electrostatic interaction between dye molecules and chitin adsorbent at pH 5. The secondary possible interactions are physical interactions between LB2R molecules and chitin, such as hydrogen bonds, van der Waals interactions, ion exchange and pore diffusions (Dhananasekaran et al., 2016).

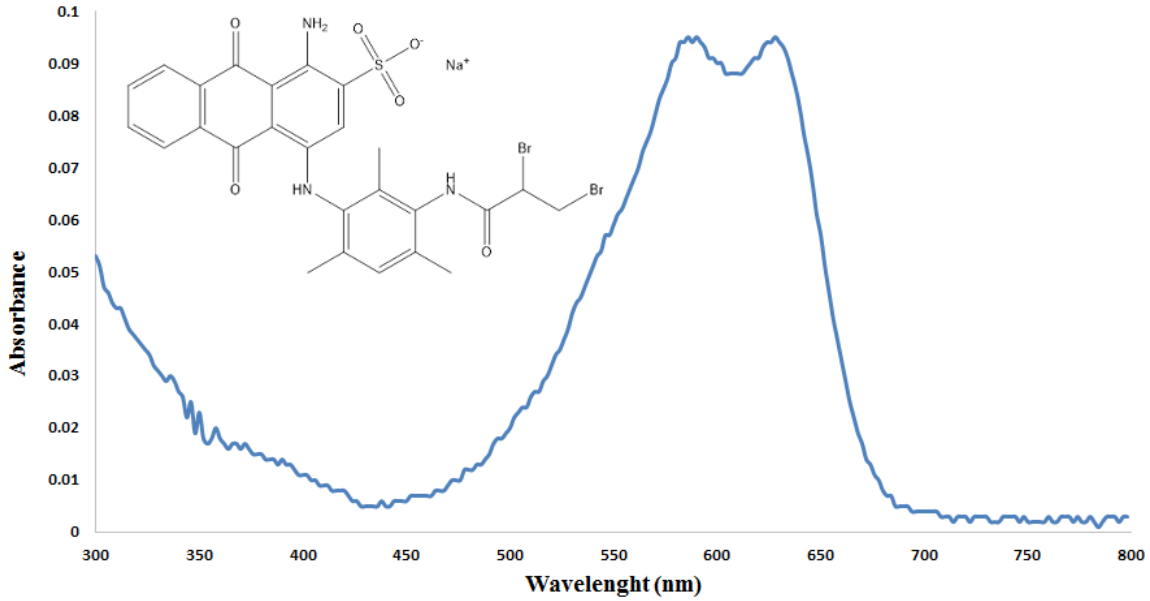

Figure 1. The UV/Vis. spectrum of LB2R textile dye illustrated with chemical structure

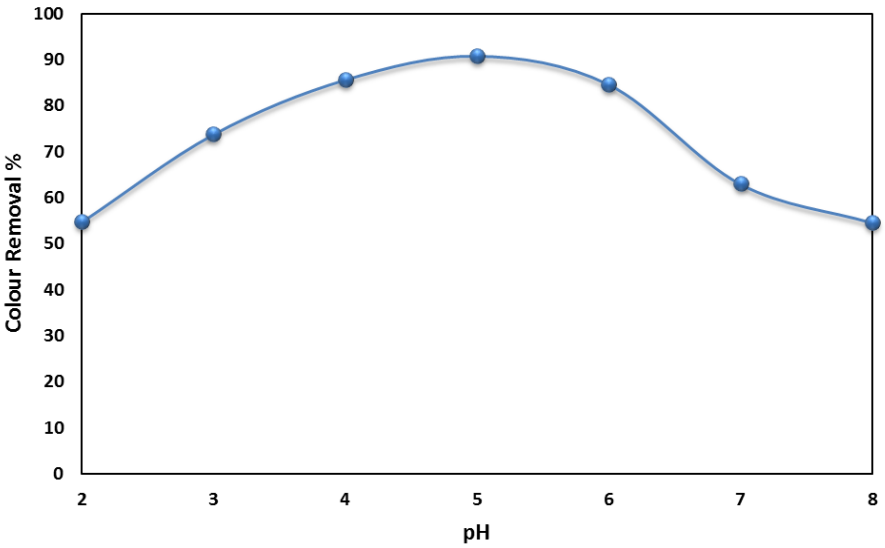

Figure 2. Effect of pH on the removal of LB2R textile dye from aqueous solution

Effect of equilibrium time

A sufficient extraction time was required to achieve the equilibrium process between LB2R analyte solution and the bio-adsorbent chitin.

The effect of the equilibrium time on the removal of LB2R by chitin were evaluated ranging from 5 to 20 minutes, at the room temperature. The results are presented in Figure 3. It is clear that the amount of adsorbed LB2R on the chitin increased with increase in time up to 17.5 min. and stood stable after this value, indicating an equilibrium state. Therefore, 20 minutes of equilibrium time was chosen as optimum.

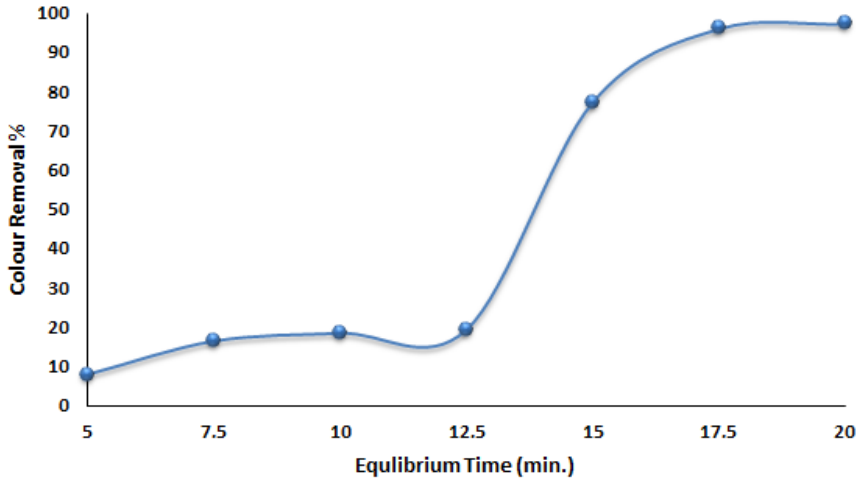

Figure 3. Effect of equilibrium time on the removal of LB2R dye from aqueous solution

Effect of bioadsorbent amount

The effect of amount of chitin bioadsorbent on the removal of LB2R was investigated in the range of 10–150 mg of chitin quantity at pH 5.0. The obtained results are depicted in Figure 4.

The quantitative LB2R removal values were obtained in the range of 100–150 mg of chitin. So a 100 mg of chitin was selected as optimum chitin amount for further studies.

The biosorbent capacity (up to 95 %) behaviour of chitin can be explained by physisorption (electrostatic interaction between oppositely charged surface and metal ions) or chemisorption (ion-exchange or chelation of metal ions) which may involve the free available lone pair of electrons on biosorbent surface.

The use of 100 mg chitin enabled 95% of dye from the solution with the initial dye concentration of 5 ppm, which was a result of active sites in the structure of adsorbent.

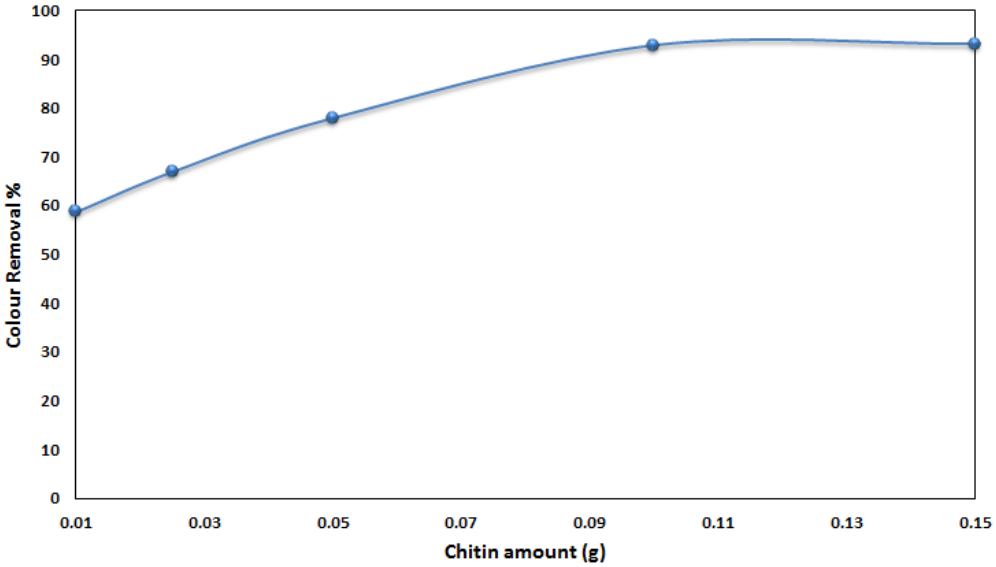

Figure 4. Effect of chitin amount on the removal of LB2R textile dye from aqueous solution

Effect of matrix ions

The interference effects of matrix ions in natural water samples is generally known as reducing the efficiency in the adsorption studies for analytes. The developed LB2R removal procedure was applied to evaluate its efficiency in the presence of different matrix ions. Obtained results are given in Table 1. The developed colour removal procedure is applicable for the separation of LB2R from water samples without interfering effects in the presence of the different ions given in Table 1.

Table 1. Effect of main interfering ions for the removal of LB2R

Ion	Added As	Concentration (µg/mL)	% Colour Removal
Na^+	$NaNO_3$	1000	96.1
K^+	KNO_3	1000	95.8
Ca^{2+}	$CaCl_2$	100	94.6
Cl^-	NaCl	1000	95.2
NO^{3-}	$NaNO_3$	250	92.7
SO_4^{2-}	Na_2SO_4	250	91.9

Applications

The presented chitin based extraction study is applied to removal and UV/Vis. spectrophotometric monitoring of LB2R textile from water samples. Addition/removal tests were performed to a natural water sample from Nigde–Turkey. The results are given Table 2. The colour removal from known added LB2R dye concentrations was used to confirm the extraction efficiency.

Table 2. The addition/colour removal studies of LB2R from a waste water sample

Added LB2R concentration (ppm)	Colour Removal (%)
-*	-
2	95.8
4	93.9
6	94.7
8	96.4
10	92.7

The obtained results in the Table 2 revealed that developed colour removal procedure is suitable for removal for LB2R textile dye from waters.

Conclusion

This study shows that the *P. fullo* chitin acted as an effective adsorbent for the removal of LB2R dye molecules from aqueous solution. The amount adsorbed dye was dependent on pH, adsorbent quantity and contact time. The dye adsorption of LB2R onto the *P. fullo* chitin was a fast process and easily reached the equilibrium in 17.5 min. So, the removal of Lanaset Blue 2R molecules in real water samples has been successfully operated. The analysis was assessed by combining the removal process and the UV/Vis. spectrophotometry. The chitin showed excellent adsorption performance for LB2R dye molecules. As a result, an effective dye adsorption method with *P. fullo* chitin as the adsorbent was established for the removal of LB2R dye from aqueous solution.

Ethical Approval

The authors declare that no need to ethical approval.

Conflicts of Interest

The authors declare that they have no conflict of interest.

Funding Statement

The authors don't declare any found.

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