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Research Article/Araştırma Makalesi

A New Approach for Dye Removal with a Polymer: Removal of Acid Orange 12 from Aqueous Solution with Shrimp Chitin

Yusuf Doruk ARACAGÖK[1], Gözde KOŞARSOY AĞÇELİ[1], Mahmut KABALAK*[1,2]

[1]*Hacettepe University, Faculty of Science, Department of Biology, 06800 Beytepe Campus, Ankara, TÜRKİYE*
[2]*Hacettepe University, Biological Diversity Research and Application Center, Ankara, TÜRKİYE*
ORCID ID: Yusuf Doruk ARACAGÖK: http://orcid.org/0000-0002-0354-0817; Gözde KOŞARSOY AĞÇELİ: http://orcid.org/0000-0001-8318-8990; Mahmut KABALAK: http://orcid.org/0000-0001-6073-2551

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Abstract: Chitin, a naturally abundant mucopolysaccharide, is the supporting material of crustaceans, insects, and etc. Chitin and its main derivative chitosan have various applications in medicine, pharmacy, biotechnology, environment, and food engineering because of their nontoxicity, biodegradability, biocompatibility, antimicrobial, and antioxidant properties. Here, research was conducted on the removal of Acid Orange 12, which is among the most used azo dyes in textiles, from aqueous solutions using shrimp chitin, a polymer. To determine the most suitable conditions, different parameters (pH degrees, amount of chitin, amount of dye, contact time) were studied. Chitin was determined to be the most efficient in removing Acid Orange 12 using pH 5 conditions. The adsorption of dye onto chitin followed the Langmuir isotherm and pseudo-second-order kinetic model.

Keywords: Arthropod, biopolymer, water, cleaning, environment.

Polimerle Boya Gideriminde Yeni Bir Yaklaşım: Karides Kitini İle Sulu Çözeltiden Asit Portakal 12'nin Giderimi

Öz Kitin, doğal olarak bol miktarda bulunan bir mukopolisakkarit olup kabukluların, böceklerin vb. canlıların destekleyici malzemesidir. Kitin ve ana türevi kitosan, toksik olmamaları, biyolojik olarak parçalanabilirlikleri, biyouyumlulukları, antimikrobiyal ve antioksidan özelliklerinden dolayı tıp, eczacılık, biyoteknoloji, çevre ve gıda mühendisliğinde çeşitli uygulamalara sahiptir. Burada, tekstilde en çok kullanılan azo boya maddelerden biri olan Asit Portakal 12'nin bir polimer olan karides kitini vasıtasıyla sulu çözeltilerden uzaklaştırılması üzerine araştırma yapılmıştır. En uygun koşulları belirlemek için farklı parametreler (pH dereceleri, kitin miktarı, boya miktarı, temas süresi) çalışılmıştır. Kitin, pH 5 koşullarında kullanılarak Asit Portakal 12'nin uzaklaştırılmasında en verimli olarak tespit edilmiştir. Boyanın kitin üzerine adsorpsiyonu Langmuir izotermine ve yalancı-ikinci-dereceden kinetik modele uymuştur.

Anahtar kelimeler: Eklembacaklı, biyopolimer, su, temizleme, çevre.

1. Introduction

Chitin is a naturally abundant mucopolysaccharide and the supporting material of arthropods. It is known to contain 2-acetamido-2-deoxy-(3-D-glucose) via a β-(1→4) linkage that is cleaved by chitinase. Despite the presence of nitrogen, its immunogenicity is extremely low. It is a highly insoluble material similar to cellulose with its solubility and low chemical reactivity. It can be considered as cellulose with hydroxyl at the C-2 position replaced by an acetamido group. Like cellulose, it naturally functions as a structural polysaccharide (Kumar, 2000). Chitin and its derivative chitosan have various implications in pharmacy, medicine, biotechnology, the environment, and the food industry due to their non-toxicity, biocompatibility, biodegradability, and antimicrobial and antioxidant properties (Kaya et al., 2016). Water pollution is at the top of the list of pollution in the world. Water resources are polluted with different substances such as organic and inorganic, heavy metals, pesticides, detergents, reactive substances, phenol, antibiotics, aromatic hydrocarbons, plastics, and dyes (Goswami et al., 2021). Water-containing pollutants adversely affect the living life in the aquatic ecosystem with the formation of odor, color change, decrease in light transmittance, and decrease in oxygen content. Pollution and odor occur not only underwater but also on the water (Sen et al., 2016). Industrial establishments using dyestuffs somehow generate wastewater with dye waste. The textile industry comes first among the industrial establishments in forming dyed water that plays a major role in reducing light transmittance. This ranking is followed by the paper, leather, and paint production industries (Katheresan et al., 2018). According to the literature, Cellulose (Liu et al., 2015; Boran, 2022) and Chitin (McKay et al., 1982) are important tools for removing dyes from water systems.

Dyes are classified differently according to their areas of use and chemical structures. Some of the dye types are acid, basic, solvent, azo, reactive, metal, indigo, natural dyes, and pigments. Azo dyes are formed by combining reactive dyes with different reactive groups and are commonly used dyes in the industry. The most distinctive feature of these dyes is that they contain one or more azo groups (such as ─N=N─, ─C≡N─) and are bound to textile fibers by covalent bonds. Azo dyes are known as the most preferred dye group with their usage of 65-70% in the world. Azo dyes used in the textile industry cause allergic

*Corresponding author: mahmut@hacettepe.edu.tr

reactions and increased hyperactivity in children. It is very important to remove these chemicals in wastewater. Acid Orange 12 dye is a kind of industrial dye that is among the azo dyes (Yadav et al., 2012; Benkhaya et al., 2020; Ajaz et al., 2020; Hameed et al., 2022; Zhou et al., 2011).

Azo dyes are recalcitrant molecules that are highly stable against oxidizing agents and resistant to aerobic decay. Therefore, they are difficult to remove from wastewater. Three different methods, physical, chemical, and biological, can be used to remove this type of paint from water. Processes such as membrane separation, aerobic/anaerobic digestion, flocculation, ozonolysis, and electrodialysis among these methods have different disadvantages such as low removal efficiency, high energy consumption, or sludge formation. On the other hand, dye removal by adsorption is a positive alternative. Different materials such as activated sludge-activated carbon, chitin, and chitosan can be used in dye removal by adsorption (Desbrières & Guibal, 2018; Millicent Mabel et al., 2019; Maderova et al., 2016; Herrera-González et al., 2019; Joshi et al., 2004; Stingley et al., 2010; Cho et al., 2015).

Our study aims to remove Acid Orange 12, an azo dye, using chitin. In the study, pH, contact time and kinetics, initial dye concentration, and chitin dose parameters were tested and the suitable conditions for adsorption were determined (Fig. 1.).

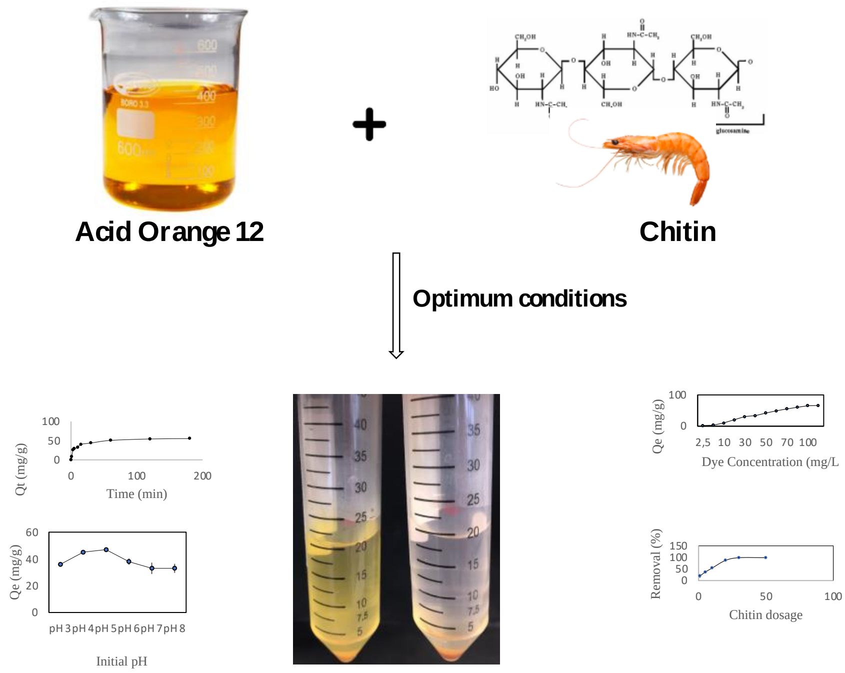

Figure 1. The removal of Acid Orange 12 from an aqueous solution by chitin

2. Material and Methods

2.1. Materials

Acid Orange 12 ($C_{16}H_{11}N_2NaO_4S$), chitin from shrimp shells, and all of the chemicals used in the study were purchased from Sigma-Aldrich (Merck).

2.2. Adsorption process

2.2.1. Determination of pH value on Acid Orange 12 adsorption

To determine the optimum pH value for dye adsorption, solutions were prepared with 20 mg of chitin and 20 mL of dye solution (50 mg/dm^3). The pH of these solutions was adjusted individually between 3.0 and 8.0. The samples were kept in a rotary shaker (150 rpm) (Mikrotest, Turkey) at 25°C for 24 hours.

2.2.2. Contact time and kinetics on Acid Orange 12 adsorption

The concentration of Acid Orange 12 in the aqueous solutions was determined using the UV–Vis spectrophotometer (Shimadzu UV-1700, Kyoto, Japan) after a certain period at 1, 3, 5, 10, 15, 30, 60, 120, 180 min.

The measurement of the dye adsorption of the polymer includes adsorption kinetics in which the reaction sequence and rate constants are evaluated. The reactions of the pseudo-first-order model and pseudo-second-order models are used to describe the dye adsorption kinetics (Hosseini et al., 2016; Aljeboree et al., 2017). In our study, the reaction rate constants were calculated with the Lagergren equation which consists of the correlation analysis between the time of Acid Orange 12 adsorbed by 1 g of chitin. The equation for a so-called pseudo-first-order kinetic model reaction is:

$$ln\ (q_e - q_t) = ln(qe) - K_1 t \quad \text{(Eq.1)}$$

The model of pseudo-second-order kinetic model reaction is:

$$t / q_t = 1 / (K_2 q_e^2) + t / q_e \quad \text{(Eq.2)}$$

2.2.3. Effect of initial dye concentration on adsorption and isotherms

The determination of the initial Orange 12 dye concentrations was studied by varying the initial dye concentration from 2.5 mg/L to 130 mg/L and by keeping the other parameters constant.

The Langmuir and Freundlich isotherm model, which is the most widely used to explain the adsorption mechanism, was used in the study. Langmuir and Freundlich's equations for these models are as follows (Huang et al., 2016):

Langmuir → $C_e/Q_e = (Q_e/Q_{max}) + (1/Q_{max}*K_L)$ (Eq.3)

Freundlich → $\ln Q_e = 1/n \ln C_e + \ln K_F$ (Eq.4)

2.2.4. Determination of chitin dose on removal rate

To determine the effect of the amount of chitin on the removal of Acid Orange 12, the amount of chitin was changed between 1 and 50 mg while keeping the pH and volume of the aqueous solution constant.

3. Results

3.1. Effect of medium pH on dye removal

The pH of the medium is the most significant parameter for removal processes. Dye adsorption was carried out in media prepared between pH 3 and 8 to monitor the effect of the initial pH of the environment where the adsorption takes place on Orange 12 (Fig. 2). Statistically, a significant difference was observed (Kruskal Wallis p-value = 0.022, Dunn's test p-value = 0.0381). As depicted in Figure 2, maximum dye adsorption occurred at low pH values (36.76-47.08 mg/g). Above pH 5, the adsorption efficiency started to decrease and the lowest efficiency was observed at pH 8. The adsorbent surface attained a positive charge under acidic conditions (Ergene et al., 2009). A previous study reported that protonated amino groups play a key role in adsorption of acidic dye with nano-chitosan particles and due to the insufficient hydrogen ion concentration, the adsorbent surface is less protonated at pH 6 value (Cheung et al., 2009).

As a result, it is considered that the electrostatic interactions between the positively charged adsorbent and the dye directly affect the adsorption capacity.

3.2. Effect of contact time and kinetics

As seen in Figure 3, adsorption takes place very quickly in the first 15 minutes and almost 75% of the biosorption capacity is reached within 30 minutes. The rapid adsorption in the first 30 minutes can be attributed to the empty binding sites on the biosorbent surface. As the contact time increases, the binding sites begins to saturate and the amount of adsorption slows down. In this study, in which chitin was used as an adsorbent, equilibrium was reached at 120 minutes.

The data obtained from the change in adsorption capacity versus time were applied to the pseudo-first-order and pseudo-second-order kinetic models. When evaluated according to the correlation coefficient, it was found that the pseudo-second-order kinetic model explained the removal of Acidic Orange 12 with chitin better than the pseudo-first-order kinetic model (Table 1).

Table 1. Kinetic constants

Pseudo-first order			Pseudo-second order		
Q_e (mg/g)	k_1 (min^{-1})	R^2	Q_e (mg/g)	k_2 (g/mg/min)	R^2
31.68	0.00025	0.971	56.49	0.0029	0.998

A previous study showed that Reactive Red 120 dye adsorption with different adsorbents followed a pseudo-second-order kinetic model (Arica & Bayramoğlu, 2007).

3.3. Effect of initial dye concentration

The dye biosorption capacity increased with the increase in the amount of Orange 12 dye in the medium and reached equilibrium at 100 mg/L dye concentration (Fig. 4). Dye adsorption capacity at equilibrium was found to be 65.75 mg/g. The increase in adsorption capacity with an increase in initial dye concentration is based on the increase in driving force for mass transfer with increasing dye concentration. However, the vacant active binding sites begin to fill and adsorption reaches equilibrium (Bayramoğlu & Yılmaz, 2018).

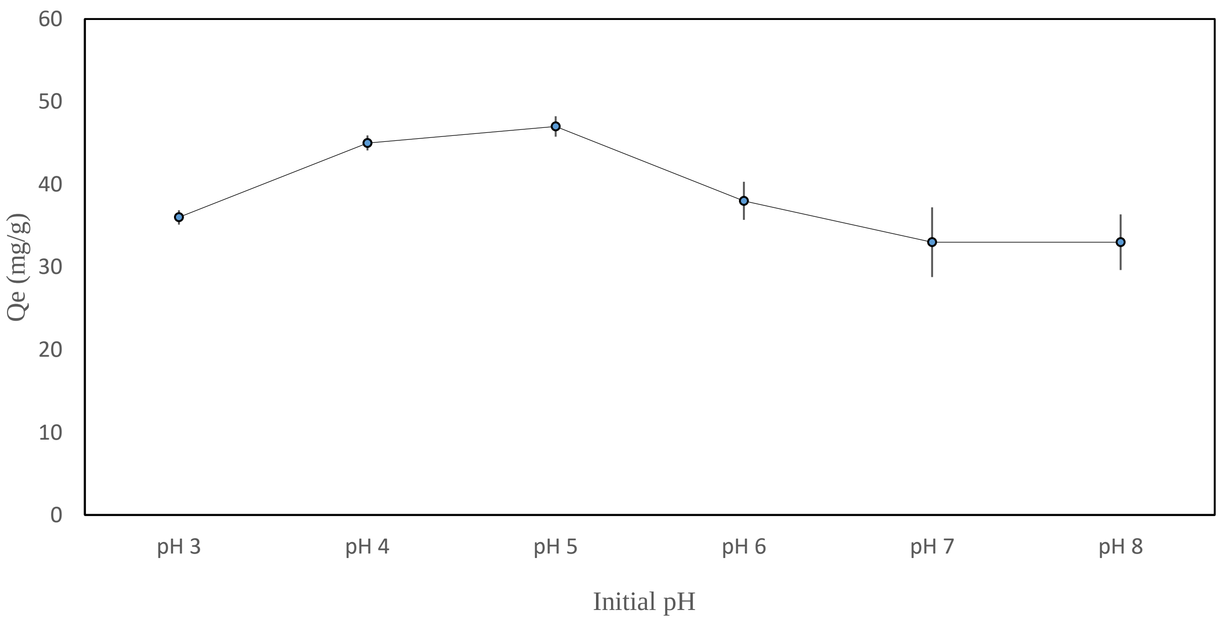

Figure 2. Effect of medium pH on dye adsorption (V: 20 ml, Biomass dosage: 20 mg, Dye concentration: 50 mg/L, Temperature: 25°C, Contact time: 24 h).

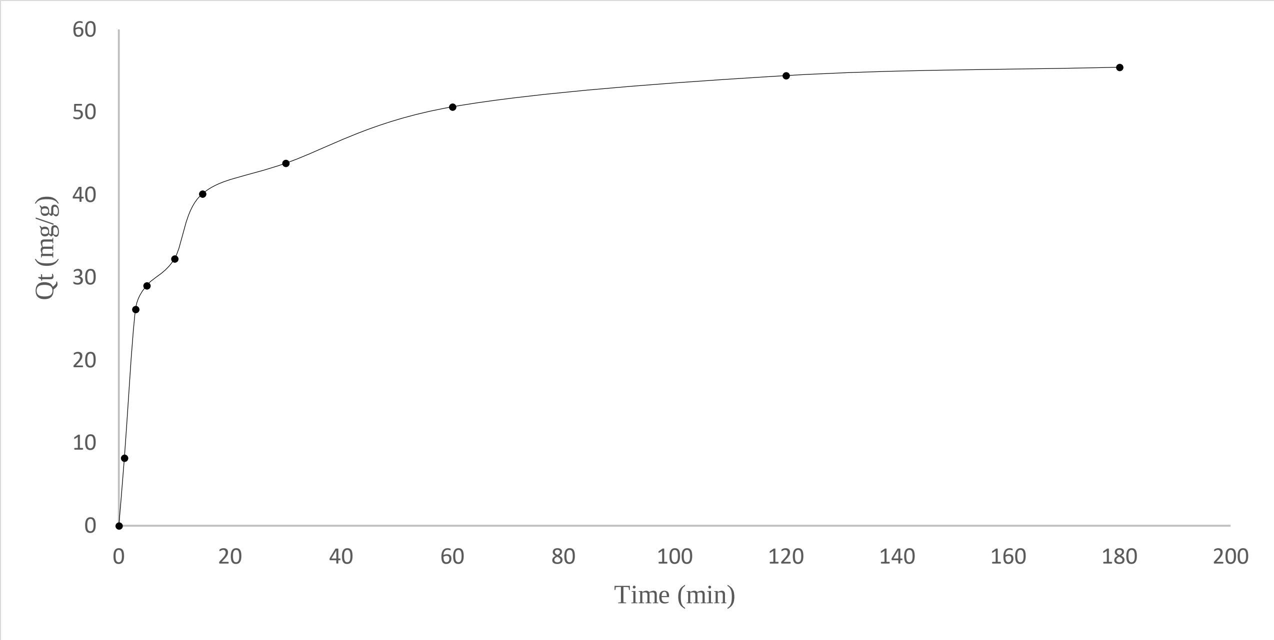

Figure 3. Effect of contact time on dye adsorption

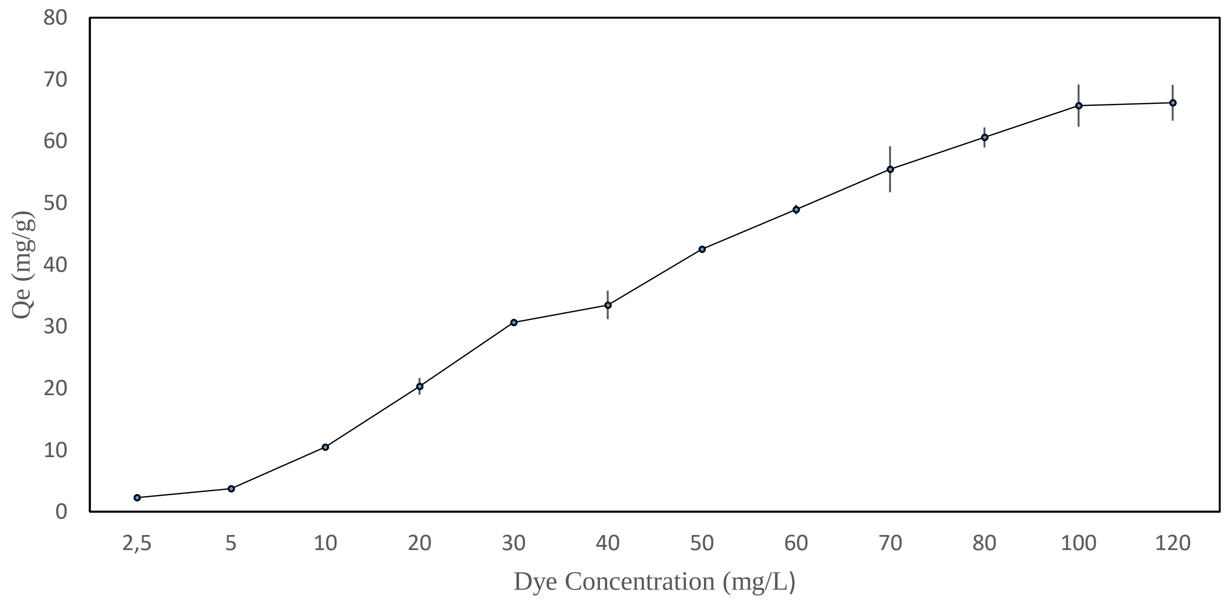

Figure 4. Effect of initial dye concentration on adsorption (V: 20 ml, Biomass dosage:20 mg, pH: 5, Temperature: 25° C, Contact time: 24 h)

3.4. Isotherms

Adsorption isotherms explain the relationship between adsorbate and adsorbent and; therefore, have great importance for the efficient use of adsorbent (Wong et al., 2003). According to our results, adsorption of Orange 12 onto chitin better fit Langmuir isotherm rather than Freundlich isotherm (Table 2). Langmuir isotherm assumes that the adsorbent has a limited number of binding sites, the binding sites are homogeneous, there is no interaction between adsorbates, and the adsorption is monolayer (Hussain et al., 2021).

The calculated Q_{max} value was found as 67.57 mg/g and the experimental value was found as 65.75 mg/g. The fact that the theoretical and experimental Qmax values are very close to each other shows the power of the isotherm model.

Table 2. The constants of isotherms

Langmuir constants			Freundlich constants		
Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	n	R^2
67.57	0.58	0.994	3.74	2.51	0.765

3.5. Effect of chitin dose on removal rate

The amount of chitin in the adsorption environment directly affected the percent removal rate. As seen in Figure 5, 98% percent dye removal was achieved with 30 mg/L chitin.

As the amount of adsorbent in the solution increases, the areas that bind the dye will increase and; as a result, the removal will increase (Ratnamala et al., 2012).

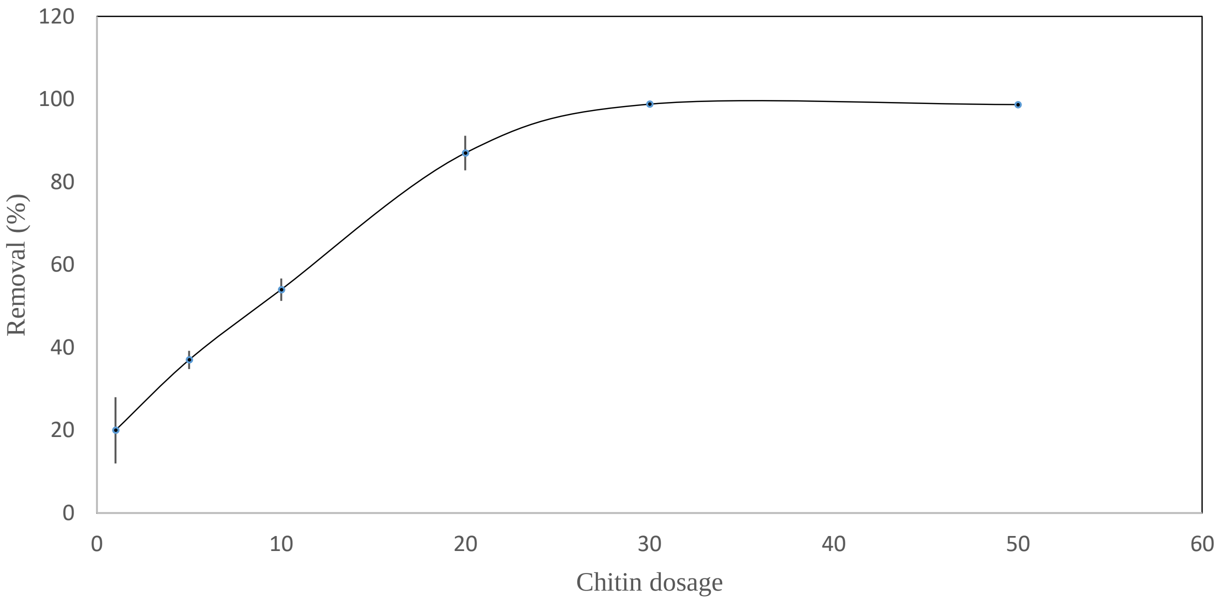

Figure 5. Effect of chitin amount on dye removal (adsorption (V: 20 ml, Dye concentration: 80 mg/L, Temperature: 25ºC, Contact time: 24 h)

4. Conclusion

In summary, this study is aimed removing dye contamination from water with chitin which is a waste obtained from shrimp shells. At different optimization conditions, Acid Orange 12 dye was removed with chitin. The most efficient condition was measured at pH 5. Equilibrium was reached in 120 minutes after rapid removal in the first 30 minutes. The dye-holding capacity of chitin increased with the increase of dye concentration in the aqueous solution and the adsorption capacity at equilibrium was measured as 65.75 mg/g. With the amount of 30 mg/L chitin, most of the dye (98%) could be removed from the aqueous solution.

We have reported for the first time the usability of chitin, which is generated as a waste but whose value is increasing day by day, in cleaning water contaminated with Acid Orange 12 dye.

Ethics committee approval: Ethics committee approval is not required for this study.

Conflict of interest: The authors declared that there is no conflict of interest.

Author Contributions: Conception – Y.D.A., G.K.A., M.K.; Design – Y.D.A., G.K.A., M.K.; Supervision – Y.D.A., G.K.A., M.K.; Fund – Y.D.A., G.K.A., M.K.; Materials – Y.D.A., G.K.A., M.K.; Data Collection or Processing – Y.D.A., G.K.A.; Analysis Interpretation – Y.D.A., G.K.A.; Literature Review – Y.D.A., G.K.A., M.K.; Writing – Y.D.A., G.K.A., M.K.; Critical Review – Y.D.A., G.K.A., M.K.

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