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Fuchsine Dye Adsorption of Surface Modified Biogenic Apatite With Tryptophan and Histidine

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ABSTRACT

In this study, the adsorption change of products obtained by chemical modification of waste fish bones, which are a biogenic-induced apathetic source, has been examined. Histidine (MH) and tryptophan (MT) were used for chemical surface modification, and cationic paint was used as fuchsine adsorbent. Paint adsorption was performed in water. The adsorption of MH and MT products was determined as 0.48 and 0.69 $mg.g^{-1}$ in 6.76 $mg.L^{-1}$ dye solution. The amount that MH and MT modified materials removed from the solution was 35.46 and 50.71%, respectively. As a result, it has been determined that the apatite-induced bones have affected the adsorption capacities of dyers as a result of different chemical molecular modifications. Additionally, it has been determined that the molecules with different qualities and properties affect the balance of adsorption. It has been observed that unprofitable products were suitable for chemical modification and adsorption procedures thanks to surface modification. With the development of studies in this field, it can be said that waste-resourced products will contribute to environmental use with effective, qualified, and useful materials.

INTRODUCTION

Today, many studies are carried out to use waste materials as convenient products in different areas. Decomposition and recycling of waste are important for nature and all living creatures. It is seen that the deficit of drinkable and available water resources in recent years makes pollution a dangerous threat for the environment and people. There are various methods used for the disposal of waste. However, it is seen that most of these methods are expensive and insufficient. Especially in recent years, most of the studies focus on converting wastes into qualified materials. Some studies were also carried out to utilize waste bones. As known, 30% of the bones are organic and the remaining 70% is the inorganic hydroxyapatite ($CA_{10}(PO_4)_6(OH)_2$, HA) forms (Narasaraju & Phebe, 1996; Kizilkaya et al., 2010; Dimovic et al., 2009). Qiu et al. (2005) synthesized nano-HA and made surface modification using lactic acid oligomer without using any catalyst. Since polylactic acid, with its mechanical force endurance, is a biocompatible and biodegradable material, studies on such polymers are focused on. Synthetic HA is synthesized by calcium hydroxide reaction along with phosphoric acid. Again, using one of the other organic stearic acid (SA), modifications were made on synthetic HA. In the modification process, changes on the surface of HA were examined using different rates from 1% to 11%. The reaction occurs with the esterification reaction between the OH groups on the surface of HA and COOH of the acid. In the study, it was observed that it was successfully modified to the HA surface and the change in the particle size distribution as a result of the modification was seen. According to the FT-IR spectrum of the SA modifications in different rates, it is clear that it comes from the aliphatic CH_3 and CH_2 groups in 2954 cm^{-1}. The peak that appears in 1548 cm^{-1} with the increase of SA aldehyde rates was determined as non-symmetrical COOC vibration bands (Li & Weng, 2008). The removal of HA cations occurs in the ion exchange of calcium ions on the surface (Banat et al., 2000; Ozawa et al., 2003; Smiciklas et al., 2006; Dimovic et al., 2009). Within the studies on natural bones, they have been especially focused on metal adsorption. In this respect, removal and adsorption of cobalt (Dimovic et al., 2009), zinc (Banat et al., 2009), chrome (Chojnacka, 2005), copper, and nickel (Alasbeb et al., 1999) were investigated. Due to the low resolution of HA in water, high stability in oxidation and reduction, high surface area, and good buffering capacity of heavy metals; it was considered as available for heavy metal sorption and reduction. In this field, synthesizing synthetic HAs; studies on the removal of cobalt (Smiciklas et al., 2006), lead (Janga et al., 2008), copper (Corami et al., 2008), and cadmium (Zhu et al., 2008) has been made. In this study, the adsorption effect of biogenic-induced fish bones in cationic dye substance removal with chemical modification was investigated.

MATERIAL AND METHODS

Materials and Chemicals

In the present study, magnetic stirrer-heater with contact thermometer (Wise Stir MSH-20D), centrifuge (Nüve NF400) and ultrasonic bath, ultra-pure water (SG, Ultra Clear 2001-B) were used. Histidine (Sigma) and tryptophan (Sigma) were used as modification chemicals. Fuchsine (Merck, 85%) was used for preparing dye solutions.

Functionalization of Bone Surfaces With Tryptophan and Histidine

The functioning of bone surfaces was carried out according to Kizilkaya et al. (2015). In the short method, fishbone particles were treated in the boiling point and inert atmosphere under the condenser with tryptophan and histidine amino acids. After refluxing, the mixture was cooled under the condenser, and the mixture was rested for 12 hours till it reached room temperature. The mixture was then centrifuged at 2000 rpm with technical water, methanol, and acetonitrile, and it was dried in the solid phase, modified by 5 times washing, at 45°C on the oven.

Cationic Dye Removal and Adsorption Methods

Fuchsine was used as the cationic dye. Measurements were made with PG Instruments Brand T80-UV / Vis spectrophotometer in the Faculty of Marine Sciences and Technology. Adsorption studies were carried out in the water with UV Spectrophotometer and measured at λ_{max} 550 nm. The fuchsine solution was treated for 24 hours with each modified product in the 1: 200 adsorbent / solvent ratio. At the end of the experiment, the adsorption change of the solution was determined with the UV spectrophotometer by filtration from the 0.45 μm syringe filter of the liquid phase from the solution.

Adsorption amount in adsorption studies is expressed as q_e and gram (G) is the amount of adsorbent adsorbed and calculated as $mg.g^{-1}$. The adsorption capacity was calculated by the following equation (1) in experimental studies (Kaushal & Tiwari, 2010; Kizilkaya et al., 2010; Rafatullah et al., 2010):

$$q_e = V \times (C_o - C_e) \times 1000 \, / \, W \quad (1)$$

q_e: The amount of adsorbed substance per unit adsorbent ($mg.g^{-1}$)

C_o: Beginning adsorbent concentration of the solution ($mg.L^{-1}$)

C_e: Adsorbent concentration remaining in the solution after adsorption ($mg.L^{-1}$)

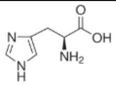
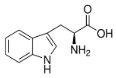
V: Volume of solution (mL)

W: Adsorbent amount

RESULTS AND DISCUSSION

In the scope of the study, the technical information of histidine and tryptophan amino acids, the adsorption capacity of the fuchsine paint adsorptions of the resulting materials (q_e) and percentages (A%) are given in Table 1. The molecular weights of histidine and tryptophan amino acids are 155 and 204 $g.mol^{-1}$, respectively. The molecular mass of the fuchsine dyer substance is 337 $g.mol^{-1}$. As a result of the experiments, cationic paint adsorption of MH and MT, bone surface-modified, was measured as 0.48 and 0.69 $mg.g^{-1}$, respectively. The bones, whose main composition is apatite, are known as the source of natural cation change. Adsorption is an event that takes place on the surface. There are many factors affecting adsorption. Foremost among them, there are factors such as surface morphology, surface properties, and surface chemistry. The adsorption process can take place with either ion exchange or surface adsorption. There are –OH groups in accordance with ion exchange in the components of apatite and bone. Positively charged hydrogen (^+H), one of these –OH groups, can cause ion exchange with the other cation groups. Thus, it can be said that the adsorption takes place with ion exchange. In this study, the -OH groups that take place on the surface of the bones –histidine and tryptophan molecules– were reacted with –COOH acid groups. Therefore, it can be said that the adsorption process takes place with the sorption effect on the molecules and surface morphology. At the end of the study, it is observed that two different chemicals affected the adsorption capacities of the bone surfaces. This effect shows the impact of the chemical on the sorption. It is considered that the reason for tryptophan having a higher capacity than histidine derives from two different chain structures in molecules and other chemical determinants.

Table 1. Information of modification chemicals and fuchsine adsorption

		Molecule	M_A	Fuchsine	
			(g.mol^{-1})	q_e (mg.g^{-1})	A %
MH	Histidine		**155.16**	0.48	35.16
MT	Tryptophan		**204.23**	0.69	50.71

It is estimated that there are colourants over 100000 in parallel with the increase in the use of textile, food, cosmetics, and many other industrial operations and many of these dyes are toxic for living creatures and the environment (Mahmoodi et al., 2011; Al-Sayed, 2011). For example, it is known that methylene blue causes burning eyes, frequent sweating, and different carcinogenic effects (Sharma et al., 2011). Therefore, it has been obligatory to remove dyer substances from water sources and industrial wastewater. Active carbon is a good adsorbent but it is not very commonly used due to its expense (Baccar et al., 2009; Mahmoodi et al., 2011). Therefore in recent years; cheap, effective, and easy to find natural resources and various industrial by-products are used and investigated instead of active carbon. Different methods are applied to remove the toxic substances present in water resources. These methods include neutralization and chemical precipitation, adsorption, ion exchange, reverse osmosis, phytoextraction, membrane and solvent extraction (Bailey et al., 1999; Donat et al., 2005). In these methods, it is known that ion exchange, chemical precipitation, membrane processes, and solvent extraction are expensive and insufficient for water with low metal content and wastewater. The adsorption process can be said as a low-cost and effective method of removal of toxic substances from water and wastewater resources.

CONCLUSION

Production and consumption of fish products in our country are known to have a wide range of space. Most of the bones from fish production facilities are not used. As a biogenic apatite source, bones are lower-cost, alternative, natural materials compared to synthetic HAPs. Hydroxyapatites can be used as an important material because of having both ion-exchange property and hydroxyl (-OH) groups. Within the scope of the project, it was investigated that the fish bones -as industrial waste- were transformed into functional materials with chemical modification. Within the scope of the study, the surface of fish-bone particles was modified with histidine and tryptophan amino acids. The materials obtained from modifications interacted with the cationic fuchsine dyer substance in the aqueous solution. The cationic dye adsorption for both modification products, MH and MT, was determined as 0.48 and 0.69 mg.g^{-1}, respectively.

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Compliance with Ethical Standards

Authors' Contributions

Both authors made contributions in each step during the preparation of the samples, conduction of the experiments, evaluation of the results, and writing the article.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

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