

EVALUATION OF THE POTENTIAL OF AGRICULTURAL WASTE PRODUCTS FOR THE TREATMENT OF TEXTILE DYE CONTAMINATED WATER

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Abstract -- In this study, the peels of waste agricultural products (banana, orange, potato) were used as biosorbent to remove textile dyes from dye contaminated water. Biosorption of the commonly used textile dye such as Acid Red P-2BX (AR) was investigated by the peels of different agricultural products. The waste peels of banana, orange and potato were prepared as dried and ash biosorbent. The effects of pH, biosorbent type, dye concentration, biosorbent dosage and temperature on dye biosorption were tested at batch scale level. The best removal of dye was performed by the banana peel. Biosorption by dried banana peel for AR dye was found to be 73.58% at optimum conditions. It was concluded that dried banana peels were effectively used in the treatment of textile dye- contaminated water.

Keywords-- Biosorption, Acid Red, Fruit Peels

I. INTRODUCTION

Recent studies reported that the textile industry effluents have been a significant source of environmental pollution due to the release of different dye compounds. The high amount of textile dyes caused environmental toxicity and public health damage (Ofomaja and Ho, 2008). The toxic effects of textile dyes in human health can be listed as irritation to the skin tachycardia, and dyspnea (Hu *et al.*, 2014). The treatment of wastewater containing textile dyes becomes an important environmental issue (Seyyedi and Mahdiyari, 2015). Therefore, environmental pollution prevention studies of waste materials have become essential to remove textile dye effluent in the environment (Keçili *et al.*, 2018). Among the methods used in wastewater treatment, biosorption is more preferred with its ease of application and high removal efficiencies (Silva *et al.*, 2018). The type of biosorbent used is one of the most decisive factors on the cost of biosorption. In wastewater treatment systems, the use of agricultural wastes (Mandi *et al.*, 2009), in particular, significantly reduces costs and increases interest in the biosorption process, which is less favorable to enterprises. Thus, different waste materials can be used as biosorbents. The textile dyes having various colors and chemical properties are treated with organic wastes such as processed cotton, soybean meal, orange peel and organic waste such as biogas sludge and powdered activated sludge (Sharma *et al.*, 2012).

Agricultural products are kind of biological materials and can be extensively found all over the world. Some studies showed that the waste peels of agricultural products such as orange peels can be effectively used in the removal of textile dyes (Hashemian *et al.*, 2013). However, there is limited knowledge about the comparison of dye biosorption by different peels of agricultural products in the literature. Also, it is stated that the use of waste peels of agricultural products in the wastewater treatment process can provide a good solution for another environmental issue such as solid waste disposal problems. Most of the agricultural products such as orange, banana, and potato are assumed as healthy food, but a lot of waste peels are produced by consumers. These waste peels are natural, abundantly available, and yearly renewable biomass sources. As solid waste materials, most of the peels are disposed of as garbage (Dai *et al.*, 2010).

The aim of this study is to investigate the textile dye (AR) removal capacity of waste banana, potato and orange peels from the aqueous solution by biosorption technique. The effects of pH, dye concentration, biosorbent amount and temperature on the biosorption were investigated experimentally. The biosorption kinetics and isotherms were also described in this study. In addition to this, the FTIR analysis was done in order to explain the dye biosorption sites on the biosorbent surface.

II. METHODS

A. Preparation of Adsorbent

The waste banana (BP), potato (PP) and orange peels (OP) were collected and, then used as biosorbent in the experiments. Two groups of biosorbent were prepared in this study. Both of the biosorbents were washed by distilled water. The first group (dried) of biosorbent was dried at 100 °C overnight and the second group (ash) was kept in the ash oven for 30 min at 500 °C. All groups were ground to make powder. To ensure that all of the powder particles were of equal size, they were passed through a 0.5 mm sieve and made ready for experiments.

B. Preparation of Dye Solution

The textile dye called Acid Red P-2BX (AR) was supplied by the textile factory in Turkey. The stock dye solutions (1000 mg/L) were prepared in distilled water and diluted to the desired concentrations for experiments.

C. Adsorption Experiments

All experiments were carried out in Erlenmeyer flasks including 100 mL of dye containing solutions. In order to determine the effect of solution pH, different pH values such as 2, 4, 6, 8 and 10 (the solution pH was adjusted using 1 M HCl or NaOH) were performed for dye biosorption. To examine the biosorbent type (dried and activated) 1 g/L of biosorbent was used in the experimental solutions. Also, the effect of initial dye concentrations, biosorbent dosage (1, 2 and 4 g/L) and temperature (25, 35 and 45 °C) was investigated in experimental series. All experimental series were done duplicate.

D. Analytical Methods

The dye concentrations in the experimental solutions were analyzed by spectrophotometer (Labomed INC. 22 model) at 535 nm. The two milliliter of samples were taken at definite times and centrifuged (Hettich EBTA12 model centrifuge) at 4000 rpm for 3 min. The supernatant was used for dye analysis.

The biosorption rate (B%) was calculated from Eqs. (1) and (2);

Biosorption rate (B%)

$$B\% = (C_o - C_f) / C_o \times 100 \quad (1)$$

$$q_m = C_o - C_f / X_m \quad (2)$$

where q_m is the uptake of dye by a unit mass of biosorbent at any time (mg/g), C_o is the initial dye concentration (mg/L), C_f is the final dye concentration at any time (mg/L) and X_m is the sorbent concentration (g/L).

E. FT-IR analysis

FT-IR analysis was done by Agilent Technologies, Cary 630 FTIR spectrophotometer. The dried biomass (before and after biosorption) were ground into powders (blended with dry spectroscopic grade powders) and, then pressed into small disks and used in FTIR measurements. Samples were scanned at the scan range of 400–4000 cm^{-1} .

III. RESULTS AND DISCUSSIONS

A. The effect of pH and biosorbent type

The pH of the solution affects the adsorption process by changing the dye ionization degree and also the mechanical interaction between the dye and ionic charge of the functional groups on the adsorbent surface. The pH effect of both dried and ash banana peel (BP), orange peel (OP) and potato peel (PP) on AR biosorption was tested at different pH (2, 4, 6, 8, 10) values. The results of the AR biosorption by the peels of dried agricultural products experiments are given in Figs. 1 and 2, respectively. Maximum dye biosorption rates and capacities occurred at pH 2 for all types of dried biosorbents. The dye biosorption rate of all biosorbents was decreased by increasing pH values (Fig. 1). Similarly, Chaleshtori *et al.* (2017) showed that Acid Red 18 dye adsorption onto activated almond shell was reduced while the pH values were increased and also reported that maximum dye removal occurred at pH 2. The highest biosorption rate of AR dye in acidic conditions depended on the electrostatic interactions between the dye ions and the positively

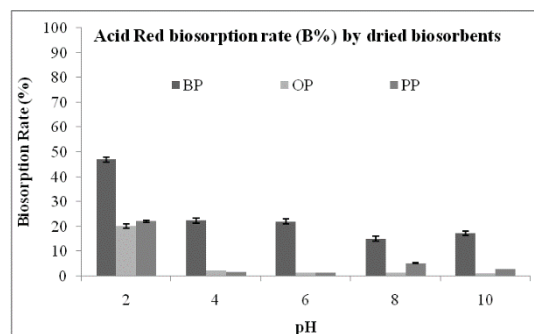


Fig. 1. The effect of pH on dye biosorption rate (B%) (BP: Banana peel; OP: Orange peel; PP: Potato peel)

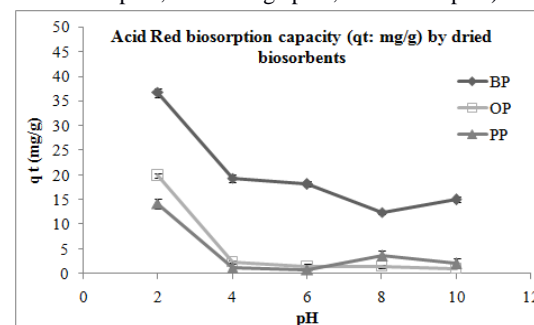


Fig. 2. The effect of pH on dye biosorption capacity (q_t) (BP: Banana peel; OP: Orange peel; PP: Potato peel)

charged biosorbent surface. The results of this study are similar to the findings of Chaleshtori *et al.* (2017). Also, Ishaq *et al.* (2014) studied the removal of dye molecules by activated carbon prepared from industrial wastes and determined that optimal pH for dye removal was 2. The results of pH effect experiments were supported by the recent studies in the literature (Ishaq *et al.*, 2014; Chaleshtori *et al.*, 2017).

In order to determine the textile dye removal potential of different waste peels of agricultural products; banana, potato and orange peels were used as biosorbents in this study. The best removal efficiency was obtained from the experiments with the banana peel. The highest biosorption capacity of the banana peel was 36.71 mg/g (Fig. 2).

AR dye biosorption rates by all dried biosorbents were decreased in the increasing pH values. Table 1 shows the AR dye biosorption capacities of all ash biosorbents at different pH values. As given in Table 1, the similar results with dried biosorbents have also been found in ash biosorbents, with an optimal pH of 2 for AR dye biosorption. Also, dried biosorbents showed better dye biosorption capacity than ash biosorbents for all peels of agricultural products. The best AR dye removal was performed by dried banana peels better than by the ash ones. In this study, the waste peels of different agricultural products were used to investigate the possibilities of their usage as biosorbents in dye removal. The dried and ash biosorbents were prepared at 100°C and 500°C, respectively. Dried biosorbents in all waste peels of agricultural product types have more effective dye biosorption rate than ash biosorbents (Fig. 2 and Table 1). In the literature, it is stated that both biosorbent stabilization and high surface area are increased at high temperatures such as 500°C (Zhao *et al.*, 2017). According to the results of this study, the biosorbent, which was dried at

100°C, achieved more successful removal compared to the ashed one in 500°C. On the other hand, Zang *et al.* (2015) showed that the increasing temperature in the results of this study caused degradation of some polymers on the cell surface and even caused the dehydration of hydroxyl groups on the surface. Recently, Zhao *et al.* (2017) reported that the pyrolysis temperature reduces the number of acidic functional groups such as carboxylic groups on the surface. The results of this study supported that the functional groups involved in dye biosorption on the surface of waste peels of agricultural products undergo thermal degradation. As a result, the biosorbent prepared at a higher temperature has a lower rate of dye biosorption. On the other hand, heating up to 500°C uses more energy than heating up to 100°C, thus preferring dried biosorbent saves energy.

The results obtained from the effect of pH and biosorbent type experiments showed that optimal pH was 2 and maximum dye biosorption capacity was performed by banana peels. Further experiments were carried out according to these findings.

B. The Effect of Initial Dye Concentration

To examine the effect of initial dye concentration on dye biosorption by dried and ash banana peels, a variety of dye concentrations (59.52, 85.05, 139.78 and 147.73 mg/L) were tested.

As given in Fig. 3, Acid Red biosorption capacity of banana peels was decreased by increasing the dye concentration up to 147.73 mg/L. The dye removal performance of dried biomass was higher than the dye removal performance of ash biomass at all dye concentrations (Fig. 3).

Table 1. The AR dye biosorption capacities (q_t ; mg/g) of all ash biosorbents at different pH values. (BP: Banana peel; OP: Orange peel; PP: Potato peel).

pH	Ash BP	Ash OP	Ash PP
	q_t (mg/g)	q_t (mg/g)	q_t (mg/g)
2	27.57	7.86	6.29
4	11.14	13.00	4.86
6	14.86	18.43	4.86
8	7.71	4.57	4.43
10	12.00	5.43	3.29

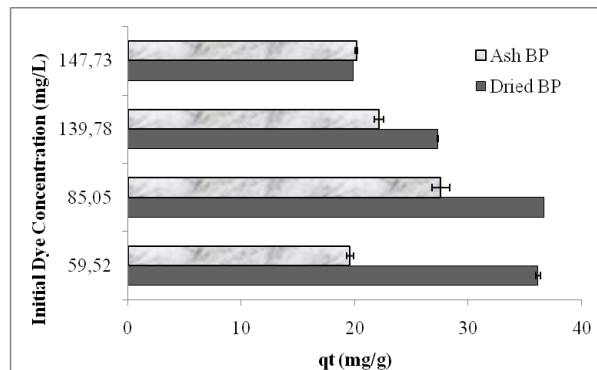


Fig. 3. The effect of initial dye concentration on dye biosorption capacity (q_t) (BP: Banana peel).

Table 2. The effect of biosorbent dosage on dye biosorption (D: dried; BD: biosorbent dosage; BP: banana peel; C_o : initial dye concentration; B: Biosorption)

D	BD (g/L)	C_o (mg/L)	Q_m (mg/g)	B (%)
BP	1	98.84	36.71	46.98
BP	2	98.84	32.71	66.18
BP	4	98.84	18.11	73.58

Maximum dye adsorption capacity was found as 36.71 mg/g at 85.05 mg/L dye concentration with a dried banana peel. Initial dye ions concentration had a driving force role to handle the mass transfer resistance between solid and liquid phases (Kaouah *et al.*, 2013). Recently, Chaleshtori *et al.* (2017) showed that Acid Red 18 removal percentage decreased with the increase in the initial dye concentration. Similarly, the augmentation in the initial AR dye concentration resulted in the decreased dye biosorption rate (Fig. 3). It is assumed that the low dye biosorption rate at high dye concentrations depends on the saturation of active sites on the adsorbent surface for dye biosorption.

C. The effect of biosorbent Dosage

The effect of biosorbent dosage on AR biosorption by dried banana peel was tested in different amounts of biosorbent (1g / L, 2g / L, and 4g / L). The results of the experiments are given in Table 2. The increasing amount of biosorbent increased biosorption efficiency (Table 2). The increasing adsorbent dosage increased the number of active sites on the adsorbent for dye sorption by the adsorbent (Shirmardi *et al.*, 2012; Kaouah *et al.*, 2013). In the results of this study, dried banana peels showed maximum dye biosorption rate (%) at the highest biosorbent content (4 g/L) as 73.58% (Table 2).

Some studies about the use of agricultural wastes as cheap adsorbents have been reported in the literature (Sharma *et al.*, 2012). Srivastava and Rupainwar (2011) used mango peel as an adsorbent for dye removal and reported that the adsorption capacity of malachite green was 0.53 mg/g. Abassi and Asl (2009) investigated the Reactive Blue 19 sorption capacity of the grape peel as an adsorbent and determined the dye removal capacity as 12.53 mg/g. Dried banana peel showed maximum dye adsorption capacity as 36.71 with 1 g/L biosorbent dosage (Table 2). The results of this study showed that the dye biosorption efficiency of banana peel was higher than the results of other studies given in the literature (Abassi and Asl 2009; Srivastava and Rupainwar 2011; Sharma *et al.*, 2012).

D. The effect of Temperature

The effect of temperature on dye biosorption was investigated at different temperature values (25 °C, 35 °C and 45 °C). The effect of temperature on AR biosorption of dried BP was found to vary with increasing temperature (Fig. 4). The AR dye biosorption rate was found as 73.58% at 25 °C, 69.42% at 35 °C and 73.48% at 45 °C by dried banana peel biosorbent (Fig. 4). There was not any significant difference between these biosorption rate values, so the dye biosorption by banana peel did not depend on the temperature of the working environment.

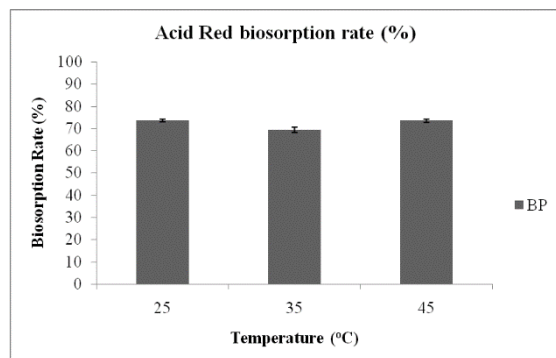


Fig. 4. The effect of temperature on dye biosorption rate (%) (BP: Banana peel).

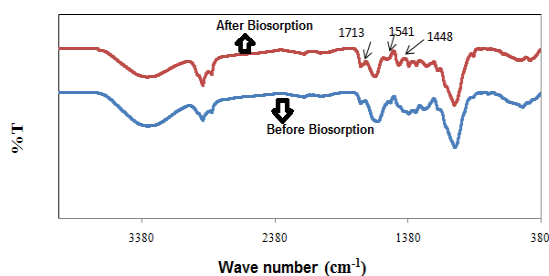


Fig. 5. FTIR spectra of banana peel before and after biosorption of AR dye.

E. FTIR

FTIR spectra before and after AR dye biosorption of the dried banana peel are shown in Fig. 5. The presence of hydroxyl groups with the peak OH voltage vibrations seen around 3400 cm^{-1} , the peaks around 2921 cm^{-1} indicates the presence of aliphatic hydrogen (CH) and the peak in 1713 cm^{-1} shows the presence of the carbonyl group (C = O). The peaks from 1541 to 1448 cm^{-1} also consist of aromatic C = C stress vibrations, showing the presence of peak C-H aliphatic methyl groups at 1370 cm^{-1} and the peak at 1230 cm^{-1} shows C-O vibrations. C-H bending vibrations in the 900 to 700 cm^{-1} range indicate the presence of aromatic structure (Özbay and Yargıç 2015).

F. Biosorption Isotherm and Kinetics

The most common isotherm models called Langmuir and Freundlich were used in this study.

The isotherm equations were calculated from Eqs. (3) and (4).

Langmuir Isotherm Equation:

$$C_e/q_e = (1/q_m)C_e + 1/K_L q_m \quad (3)$$

Freundlich Isotherm Equation:

$$\ln(q_e) = \ln(K_F) + 1/n \ln(C_e) \quad (4)$$

In these equations; q_e is the amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg/g), q_m is the maximum dye uptake per unit mass of adsorbent (mg/g), K_L is the Langmuir isotherm constant (L/mg) and K_F is the Freundlich isotherm constant (L/mg).

In order to examine the dynamics of the biosorption process in terms of the theoretical q_e values and order of rate constant, pseudo-first-order and pseudo-second-order kinetic model equations were used. Kinetic data were calculated with the equations of pseudo-first-order (Eq. 5) and pseudo-second-order (Eq. 6) kinetic models.

Table 3. Biosorption isotherm parameters for the biosorption of AR on a dried banana peel (q_m : the maximum AR uptake per unit mass of adsorbent, K_L : Langmuir isotherm constant; K_F : Freundlich isotherm constant)

Langmuir		
q_{max} (mg/g)	K_L (L/mg)	R^2
4.427	0.03967	0.839
Freundlich		
K_F (L/mg)	$1/n$	R^2
423.27	0.226	0.877

Table 4- Kinetic parameters for the biosorption of AR onto the dried banana peel (q_{ecal} : The theoretical adsorption capacity; q_{exp} : The experimental adsorption capacity; k_1 : rate constant of the pseudo-first-order kinetic model, k_2 : rate constant of the pseudo-second-order kinetic model)

Pseudo-first-order model			
q_{ecal}	q_{exp}	k_1	R^2
0.0862	18.10	0.000	0.737
Pseudo-second-order model			
q_{ecal}	q_{exp}	k_2	R^2
11.236	18.10	0.001286	0.975

Pseudo first-order kinetic model equation:

$$\log(q_e - q_t) = -k_1/2.303t + \log q_e \quad (5)$$

Pseudo second-order kinetic model equation:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \quad (6)$$

In these equations q_e is the adsorption capacity, k_1 is the rate constant of pseudo-first-order kinetic model and k_2 the rate constant of pseudo-second-order kinetic model.

Biosorption isotherm and kinetic models were calculated at maximum decolorization environment with optimal conditions. The Langmuir and Freundlich isotherm correlation values were calculated as 0.839 and 0.877 for the biosorption of dye, respectively (Table 3). The biosorption was suitable with the Freundlich isotherm model due to the highest correlation value. Previously, Shirmardi *et al.* (2012) stated that the adsorption of Acid Red 18 dye on activated charcoal prepared from the almond shell. Freundlich isotherm model is based on a slower increase after by the reach of saturation on the adsorbent surface with the increasing amount of adsorbed material at the beginning (Mandi *et al.*, 2009). Freundlich isotherm model also explained for the heterogeneous surface energy systems.

The calculations about biosorption kinetics are given in Table 4. The correlation value of the pseudo-second-order model was the highest as 0.975, so the biosorption of AR on the dried banana peel biosorbent was fitted with the pseudo-second-order kinetic model. Similarly, Mahmoud *et al.* (2014) reported that the kinetic model of manganese biosorption on banana peel obeyed with the pseudo-second-order model. Also, Chaleshtori *et al.* (2017) recently reported the similar results with this study and showed the pseudo-second-order kinetic model

was compatible with the adsorption of Acid Red 18 dye on activated charcoal prepared from the almond shell. Pseudo-second-order kinetic model is considered as the sorption includes a second-order mechanism via chemisorptions by the means of rate-limiting step (Tutu *et al.*, 2013).

IV. CONCLUSION

The waste banana peel performed high adsorption capacity of textile dye and the optimal conditions were determined in this study. As a result of the experiments carried out, it was suggested that the waste dried banana peel, which was easy to obtain and cheap, could be used in the removal of dyes in the laboratory scale experiments of the biosorption method. The decolorization technologies can use the waste banana peel as a biosorbent in the industrial scale areas.

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