

Treatment of Polluted Aqueous Solutions with different types of Dyes by Eggplant Peels Accessing to Zero Residue Levels

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ABSTRACT

This paper is related to study the potential of eggplant peel (EP) to remove nine types of dyes (which were acid orange, brilliant green, Congo red, crystal violet, direct black, direct brown, indigo carmine, methylene blue, and yellow dye) from simulated synthetic aqueous solutions (SSAS) using immobilized Polyphenol Oxidase (PPO) enzyme extracted from EP and adsorption process. Results show high ability of PPO to remove dyes with an efficiency reach to 99%. The residue from PPO extraction from EP was investigated to remove the same dyes as adsorbent media. Higher removal efficiency were (93.15, 95.25, 92.55, 94.75, 92.85, 94.65, 90.25, 91.35 and 93.40)% for acid orange, brilliant green, Congo red, crystal violet, direct black, direct brown, indigo carmine, methylene blue, and yellow dye respectively.

Keywords : Eggplant Peel, Dyes, PPO, Adsorption, Residue and ZRL

I. INTRODUCTION

Several metiers predominantly employ dyes and tinctures to tint their manufactures, like food, textile and lather industries, biological research, paper production, photochemical cell, hair colourings, etc. [1]. Most dyes are apparent in aqueous systems at very minimum concentrations nearly (1 mg.l⁻¹). Between (10-200 mg.l⁻¹) is the range of the concentration of dyes in the wastewaters produced from textile industries. Defilement due to the use of dyes may compose a serious risk because of the enormous amount release. The discharge of the wastewaters of dyes to the open waters may present hazardous problems. In addition to the undesirable aesthetic problems to the water user, the International Agency for Research on Cancer (IARC) has categorized many kinds of dyes like benzidine as being related with the cancer in humans [2]. The treatment of wastewaters effluents produced from textile industries using

classical chemical, physical and biological methods are very difficult issue. Adsorption technology may be an effective method for treating different types of water pollutants like odours, suspended solids, oil, and organic matter [3]. The most widely adsorbent used in adsorption method was activated carbon due to its ability to adsorb many metallic ions and organic matters, but it's used is decreased now day because the expensive cost required. So, cheaper materials instead of activated carbon must be found [4]. Many substitutes like rice husk, sugarcane bagasse, fly ash, sludge ash, bituminous coal, maize cob, coconut shell, wheat straw, cotton waste, groundnut shell, and orange peel have been proposed as an adsorbent for various types of dyes [5-14]. The aim of this investigation is to test the ability of using Eggplant Peel wastes in two ways for adsorption removal of various dyes which are acid orange, brilliant green, Congo red, crystal violet, direct black, direct brown, indigo carmine, methylene blue, and yellow dye from

aqueous solutions. The first method is conventional adsorption of dyes using originally Eggplant Peel and the second is removing the same types of dyes using extracted Poly Phenol oxidase enzyme from mature Eggplant Peel and comparison between the two methods accessing to zero residues level (ZRL).

II. EXPERIMENTAL WORK

A. Eggplant Peel (EP)

Eggplant Peel (EP), mature eggplant with black peel outside, was collected from local market in Baghdad. The EP was washed three times with excess double distilled water and boiled to remove dust, impurities and other fine dirt particles that may be attached to the EP. The washed EP was cut into small pieces (0.5-1 cm) after that and then dried at 50°C for 24 hours.

B. Preparation of Crude Poly Phenol Oxidase (PPO)

Enzyme Extract from Potato Peel (PP)

EP (100g) was cut into small pieces and homogenized by using (200 ml) of prechilled (4°C) containing 0.1 M sodium phosphate buffer extraction buffer (pH 6.5), Poly vinyl pyrrolidone (PVP) and Triton X-100 using blender for 1 minute at maximum speed. The slurry was centrifuged at 9000 rpm at 4°C for 15 minutes. The supernatant obtained was filtered under vacuum from a buncher funnel containing Whitmann® No. 1 filter paper and the filtrate was collected in a conical flask. Then, 100 ml of the filtrate was pipette drop by drop into (200ml) of cold acetone (- 20°C) for the formation of the precipitates. The crude PPO precipitates separated by centrifugation at 10,000 rpm at 4°C for 15 minutes. The resultant light brown coloured acetone precipitates was dried overnight at room temperature. The acetone powder that obtained was stored at (- 20°C). The enzyme extraction from acetone powder was conducted by mixing 0.1g acetone powder, 15 ml of prechilled 0.1M sodium phosphate buffer, pH 6.5 and stirring for 1 hour at 4°C with a magnetic stirrer. The temperature was maintained by covering the beaker with aluminium foil and was enclosed with ice surrounding the beaker. The obtained crude extract was filtered through

cheese cloth and the filtrate was centrifuged at 10,000 rpm for 30 min. The supernatant was discarded and used as crude PPO [15,16].

C. Enzyme Assay

The assay solution was prepared by mixing 1 ml of 20 mM substrate (L-DOPA), 1 ml 0.2M sodium phosphate buffer, 0.9 ml H₂O and 0.1 ml of enzyme solution. Enzyme activity was measured spectrophotometrically at 475 nm against a blank containing no enzyme. One unit of enzyme activity is defined as the amount of enzyme that transforms 1 μmole of substrate Levodopa (L-DOPA) (L-3,4-dihydroxyphenyl-alanine) per minute under assay conditions [15].

D. Preparation of Zeolite from Rice Husk as a Carrier for PPO

Rice husk (which was a raw material for zeolite type Y catalyst synthesis) firstly treated with 10% phosphoric acid (H₃PO₄) for 24 hours. Then they were well washed with double distilled water, filtered, dried in air, and calcined at 750°C for 6 hours. 12 g of calcined rice husk were then subjected for dissolution in sodium hydroxide NaOH (4 M) followed by refluxing at 90°C for 12 hours. After that concentrated hydrochloric acid (HCl (37%)) was added to the aforementioned base dissolved rice husk for complete precipitation. Rice husks were filtered, washed with excess distilled water to be freeing from chloride ions and finally dried in an oven at 120°C for 6 hours. Zeolite type Y was synthesized using prepared rice husk above as a silica source in the following method. A 500 ml Teflon beaker containing a magnetic stirrer was washed with deionized water. Sodium hydroxide of 1.6616g was added slowly to deionized water and stir until clear and homogenous solution appeared for about 5 minutes. The aqueous solution of sodium hydroxide was ready for the preparation of seed gel. The gel was prepared according to the following molar chemical composition: 10.67 Na₂O: Al₂O₃: 10 SiO₂: 180 H₂O. Two millilitres aqueous solution of sodium hydroxide

was added to 0.7515g sodium aluminate oxide until a homogenous mixture was formed; 1.5361g of prepared rice husk above was added separately to 5.5 ml sodium hydroxide aqueous until mixed homogeneously. Both of the preparations were heated under vigorous stirring to obtain a homogenous mixture. The sample was aged for 24 hours at room temperature in the Teflon bottle. The aluminate and silicate solutions were mixed together in the polypropylene beaker, subsequently stirred for 2 hours with the purpose of making it completely homogenized. This combined solution was used as the feed stock gel. The synthesized zeolite type Y which was in sodium (Na⁺) powder form. In order to make a promoted HY-zeolite catalyst ready for test in any process, hydrogen zeolite (HY-zeolite) form must be prepared. The HY-zeolite was prepared by exchanging Na⁺ ions in the sodium form zeolite type Y with ammonium chloride solution NH₄Cl. In order to obtain ideal degree of ion exchange the technique of multi-steps (three times repeating) was used. Thus, the first step, 2N of ammonium chloride solution (26.75 g of NH₄Cl in 250 ml of distilled water) contacted with 90 g of prepared NaY-zeolite with stirring for 2 hours. In the second step, the procedure in the first step was repeated under the same conditions but on about 60 g of zeolite, which was taken from the total zeolite amount produced in the first step. Finally, in the third step, the procedure under the same conditions was repeated again but on about 30 g of zeolite, which was taken from the total zeolite amount produced in the second step. The exchanged ammonia zeolite were filtered off, washed with deionized water to be free of chloride ions dried overnight at 120°C and then calcined initially at 150°C for two hours. The temperature was increased 75°C per hour until it reached 550°C and it was held constant for 5 hours at this temperature. During calcination, ammonia and water were liberated and HY-zeolite was formed [17].

E. PPO Immobilization in zeolite type Y

A 25 g of prepared HY-zeolite powder (prepared in section 6.2 above) was used for the immobilization of PPO in HY-zeolite. Immobilization solution of PPO was achieved by adding 10 mg of NaY-Zeolite carrier to 10 ml 0.05 M sodium phosphate buffer (pH 7.0) and mixing with 40 mg of crude PPO enzyme prepared. Mixture was left over night on shaker at 600 rpm at 4°C. Biocatalyst (enzyme and support) was taken out from solution, centrifuge at 10000 rpm and washed six times in 20 ml 0.05 M sodium phosphate buffer to remove free PPO enzyme. The removed biocatalyst was finally stored in 0°C [18].

F. Stock solutions

In order to avoid interference with other elements in wastewater, the experiments in this study were carried out using simulated synthetic aqueous solution (SSAS) of different dyes concentrations. 1000 mg/l stock solution of dyes was prepared by dissolving known weight of four types of dyes which were acid orange, brilliant green, Congo red, crystal violet, direct black, direct brown, indigo carmine, methylene blue, and yellow dye (each one alone) in one liter of double distilled water, all solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work of this investigation. The dyes concentrations were measured using spectrophotometer thermo – genesys 10 UV, USA.

G. Application of immobilized PPO (biocatalyst) using sorption unit

Adsorption unit shown in Figure 1 was used to study the potential of immobilized PPO (biocatalyst) to remove different types of dyes from SSAS. The operating conditions used in this study were temperature, pH, flow rates of SSAS of dye (each type alone), initial feed concentration and height of biocatalyst bed are constant at 25°C, 7, 5 ml/min and 1 m respectively, and initial feed concentrations of SSAS of different dyes which are varied between (50-100) mg/l. Outlet samples after treatment in each

experiment were collected every 10 minutes from the bottom of packed column and the remaining dyes concentration in SSAS was detected spectrophotometrically. The results show the ability of prepared biocatalyst to remove dyes from SSAS in different concentrations with removal efficiency range between 97.43 to 99.75% for 50 mg/l initial concentration as shown in Figure 2.

H. Sorption Unit

Fixed bed column of continuous mode experiments were conducted in order to test nine types of dyes (acid orange, brilliant green, Congo red, crystal violet, direct black, direct brown, indigo carmine, methylene blue, and yellow dye) removal by treated SSAS of above dyes each one alone at desired concentration with the various bed heights of the adsorbent media (EP waste remaining from extraction of PPO enzyme) using different flow rates of SSAS of nine types of dyes at various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. A schematic representation of the sorption unit is shown in Figure 2 where the flow direction is downward by gravity. The sorption unit consists of two glass container of SSAS of dyes one for inlet and another for outlet each of (1 liter) capacity. Glass column has 2.54 cm ID and 150 cm height. The sorption column packed with adsorbent media to a height of (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm) supported from the top and the bottom by glass hollow cylinder layer, each cylinder have (0.5 cm ID, 0.1 cm thickness and 1 cm long). Before starting the runs, the packed bed sorption column was rinsed by double distilled water down flow through the column. The EP is packed in the column to the desired depth, and fed to it as slurry by mixing the media EP with distilled water in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was accommodation and putting the required amount of adsorbent media, the adsorption process started by allowing the dyes SSAS of required concentration and pH down flow through the sorption column from inlet container by gravity at a

precise flow rate in experiment which is adjusted by the valve as shown in Figure 2. To determination the best operational conditions, the experiments were carried out at a temperature between (5–45°C), various pH values which are (1–8) and initial feed concentrations of SSAS of different dyes which are between (1–100) mg/l each one alone and at different flow rates which are between (5–100) ml/min for dyes initial feed concentration. Outlet samples after treatment in each experiment were collected every 10 minutes from the bottom of packed column and the unadsorbed concentration of dyes in SSAS was analyzed by spectrophotometer.

III. MATHEMATICAL MODEL

Fixed bed dynamics are describing by a set of convection-diffusion equations, coupled with source terms due to adsorption and diffusion inside adsorbent particles. Inside the particle, molecules of adsorbate diffuse into the inner portions of particle via surface diffusion, pore diffusion, or both. The solution of these equations will give rise to the prediction of the needed concentration distribution. This investigation focuses on understanding the mechanism of both surface diffusion and pore diffusion. To formulate a generalized model corresponding to the dispersion flow, surface diffusion and pore diffusion mechanism, following assumptions are made:

The system operates under isothermal conditions.

1. The equilibrium of adsorption is described by Langmuir isotherm.
2. Intraparticle mass transport is due to Fickian diffusion, and it is characterized by the pore diffusion coefficient, D_p and the surface diffusion, D_s .
3. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient, k_f .
4. Film transfer resistance for mass transport from the mobile to the stationary phase.

5. Local adsorption equilibrium between the adsorbate adsorbed onto the adsorbent surface and the adsorbate in the intraparticle stagnation fluid.
6. Both surface and pore diffusion are included in the mass transport mechanism Axial dispersion.

Equations used in simulation technique represent a set of simultaneous, nonlinear, partial differential equations (PDEs) that can be solved numerically. The discretization was applied to space coordinates (Z and r) to convert the PODs to a set of ordinary differential equations (ODEs). The resulting ODEs can be solved using an existing ODE solver provided by MATLAB [19].

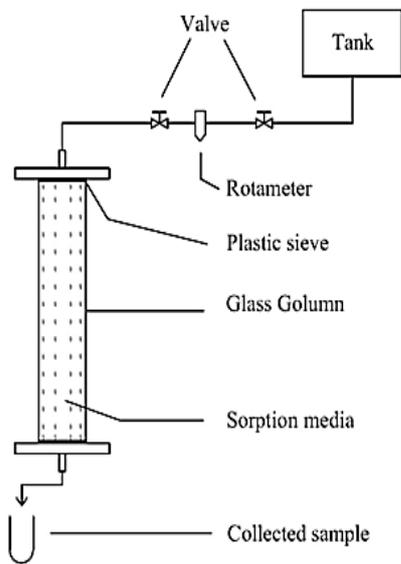


Figure 1. Setup for the Adsorption Unit

IV. RESULTS AND DISCUSSION

The ability of EP to remove dyes from SSAS in fixed bed column of continuous mode at various parameters which are pH's of SSAS of dyes (pH), height bed of adsorbent media EP (l), flow rates of SSAS (F), SSAS temperature (T_{feed}) and time of treatment (t) was investigated. The experiments were achieved by varying all above parameters for different initial concentrations (C₀) of SSAS of dyes. Thus, the results obtained are explained below.

A. Effect of Initial Concentration

The results showed IN figure 2 that using adsorbent material, the percent removal of dyes was decreased when the initial concentration (C₀) of SSAS of dyes was increased at constant other variables as shown in Figure 3. This can be explained by the fact that the initial concentration of dyes had a restricted effect on dyes removal capacity; simultaneously the adsorbent media had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of dyes molecules competing for the available functions groups on the surface of adsorbent material. Since the solution of lower concentration has a small amount of dyes than the solution of higher concentration of it, so the percent removal was decreased with increasing initial concentration of dyes. For adsorbent media, higher percent removal were (93.15, 95.25, 92.55, 94.75, 92.85, 94.65, 90.25, 91.35 and 93.40) % for acid orange, brilliant green, Congo red, crystal violet, direct black, direct brown, indigo carmine, methylene blue, and yellow dye respectively at initial dyes concentration of 1 mg/l, so adsorbent material was found to be efficient to dyes removal from SSAS and wastewater.

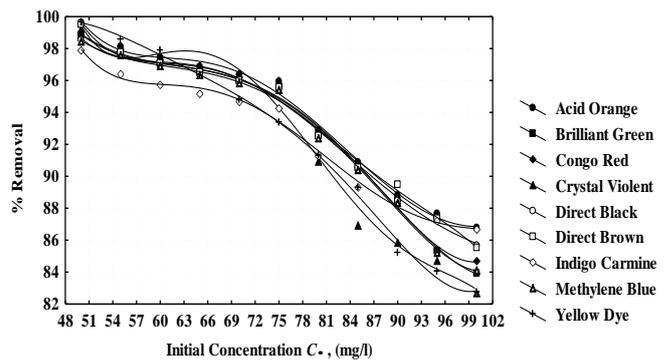


Figure 2. Effect of initial concentration (C₀) on the percent removal of different types of dyes using biocatalyst @ T=25°C, pH=7, and t=60 min

B. Effect of pH

The results showed in figure 3 that using adsorbent material, the percent removal of acid orange, Congo red, direct black, direct brown and indigo carmine

were decreased when the pH of SSAS was increased at constant other variables, while the percent removal of brilliant green, crystal violet methylene blue, and yellow dye were increased when the pH of SSAS was increased at constant other variables as shown in Figure 4. It is well recognized that the pH of the aqueous solution is an important parameter in affecting adsorption of dyes. High adsorption of acid orange, Congo red, direct black, direct brown and indigo carmine at low pH can be explained in both terms; the species of these dyes and the adsorbent surface. For this case, at low pH, i.e. acidic conditions, the surface of the adsorbent (EP) becomes highly protonated and favours adsorb of above group of the dyes in the anionic form. With increasing the pH of SSAS, the degree of protonation of the EP surface reduces gradually and hence adsorption is decreased. Furthermore, as pH increases there is competition between hydroxide ion (OH^-) and species of acid orange, Congo red, direct black, direct brown and indigo carmine, the formers being the dominant species at higher pH values. The net positive surface potential of sorbent media decreases, resulting in a reduction the electrostatic attraction between the (sorbent) Congo red species and the (sorbate) adsorbent material surface (EP), with a consequent reduced sorption capacity which ultimately leads to decrease in percentage adsorption of acid orange, Congo red, direct black, direct brown and indigo carmine dyes. In the other hand, the adsorption of brilliant green, crystal violet methylene blue and yellow dye (each one alone) can be explained by ion-exchange mechanism of sorption in which the important role is played by functional groups that have cation exchange properties.

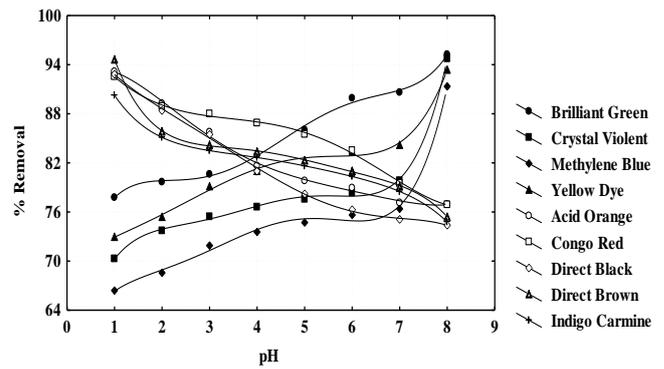


Figure 3. Effect of pH on the percent removal of dyes @ $C_0 = 1 \text{ mg/l}$, $T_f = 45^\circ\text{C}$, $l = 1 \text{ m}$, $t = 60 \text{ min}$, and $F = 5 \text{ ml/min}$

For this case at lower pH values, dyes removal was inhibited, possibly as a result of the competition between hydrogen and dyes molecules on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligand functional groups in adsorbent media (EP) would be exposed, increasing the negative charge density on the adsorbent material surface, increasing the attraction of dyes molecules with positive charge and allowing the sorption onto adsorbent material surface [20].

C. Effect of Adsorbent Media Bed Height

The results elucidated that when the adsorbent media bed height was increased, the percent removal of dyes was increased too at constant other variables as shown in Figure 4. The increased of bed height (l) meaning increased in the amount of adsorbent media EP, thus increasing the surface area of adsorbent material, hence increased the number of active sites in the adsorbent material surface i.e. increased the availability of binding sites for adsorption and consequently increase dyes removal capacity on EP. This lead to increase the ability of adsorbent media to adsorb greater amount of dyes from SSAS at different initial concentrations and ultimately the percent removal of dyes increased.

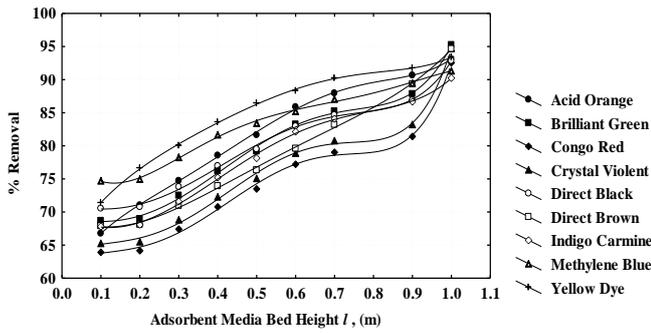


Figure 4. Effect of adsorbent media bed height (l) on the percent removal of dyes @ $C_0 = 1$ mg/l, pH=1 or 8, $T_f = 45^\circ\text{C}$, $t = 60$ min, and $F = 5$ ml/min

D. Effect of Flow Rate

The results illustrated that when the flow rate of SSAS of dyes was increased, the percent removal of dyes was decreased at constant other variables as shown in Figure 6 This may be due to the fact that when the flow of SSAS of dyes increasing, the velocity of solution in the column packed with the adsorbent media EP was increasing too, so the solution spend shorter time than that spend in the column while at low flow rate, the SSAS of dyes resides in the column for a longer time, and therefore undergoes more treatment with the adsorbent media, thus the adsorbent media uptake low amount of dyes from SSAS of dyes for high flow rate, therefore the percent removal of dyes was decreased when the flow rate was increased.

E. Effect of Feed Temperature

The results demonstrated that when the temperature of feed which was SSAS of dyes was increased, the percent removal of dyes was increased too at constant other variables as shown in Figure 5. The effect of temperature is fairly common and increasing the mobility of the acidic ion. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the adsorbent media enabling dyes ions to penetrate further. It was indicated that dyes adsorption capacity increased with increasing feed temperature from 5 to 45°C . This effect may be

due to the fact that at higher temperature an increase in active sites occurs due to bond rupture.

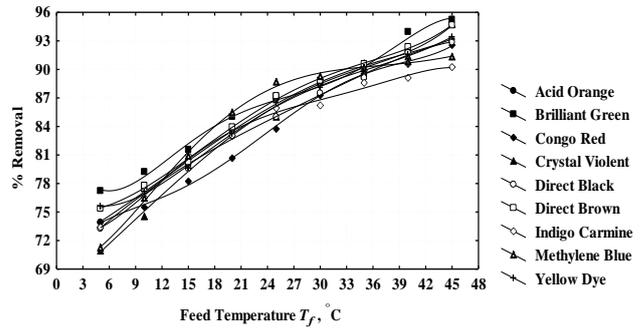


Figure 5. Effect of feed temperature (T_f) on the percent removal of dyes @ $C_0 = 1$ mg/l, pH=1 or 8, $l = 1$ m, $t = 60$ min, and $F = 5$ ml/min

F. Effect of Treatment Time

The results demonstrated that when the treatment time of SSAS of dyes increased the percent removal of dyes increased at constant other variables as shown in Figure 8. This may be due to the fact that when the time of treatment of SSAS of dyes increasing and the velocity of SSAS in the column packed with the adsorbent material was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the adsorbent material uptake more amount of dyes from SSAS, therefore the percent removal of dyes from SSAS was increased.

Figure 3 Effect of initial concentration (C_0) on the percent removal of dyes @ $T_f = 45^\circ\text{C}$, $l = 1$ m, pH=1 or 8, $t = 60$ min, and $F = 5$ ml/min

Figure 4 Effect of pH on the percent removal of dyes @ $C_0 = 1$ mg/l, $T_f = 45^\circ\text{C}$, $l = 1$ m, $t = 60$ min, and $F = 5$ ml/min

Figure 5 Effect of adsorbent media bed height (l) on the percent removal of dyes @ $C_0 = 1$ mg/l, pH=1 or 8, $T_f = 45^\circ\text{C}$, $t = 60$ min, and $F = 5$ ml/min

Figure 6 Effect of aqueous solution flow rate (F) on the percent removal of dyes @ $C_0 = 1$ mg/l,

pH=1 or 8, $T_f=45^\circ\text{C}$, $l = 1 \text{ m}$, and $t=60 \text{ min}$

Figure 7 Effect of feed temperature (T_f) on the percent removal of dyes @ $C_o = 1 \text{ mg/l}$, pH=1 or 8, $l = 1 \text{ m}$, $t=60 \text{ min}$, and $F=5 \text{ ml/min}$

Figure 8 Effect of treatment time (t) on the percent removal of dyes @ $C_o = 1 \text{ mg/l}$, $T_f=45^\circ\text{C}$, pH=1 or 8, $l = 1 \text{ m}$, and $F=5 \text{ ml/min}$

V. CONCLUSIONS

The following conclusions can be drawn:

There is ability remove high concentrations of dyes (between 50-100 mg/l) by extract PPO enzyme from eggplant peel, loaded it on the prepared biocatalyst (zeolite type Y) and treated the wastewater containing dyes.

Waste EP remaining from PPO extraction showed a good ability to remove dyes too, from SSAS using fixed bed adsorption unit. Higher percent removal was (93.15, 95.25, 92.55, 94.75, 92.85, 94.65, 90.25, 91.35 and 93.40) % for acid orange, brilliant green, Congo red, crystal violet, direct black, direct brown, indigo carmine, methylene blue, and yellow dye respectively at initial concentration of 1 mg/l, so waste EP adsorbent material was found to be efficient to remove dyes from SSAS and wastewater.

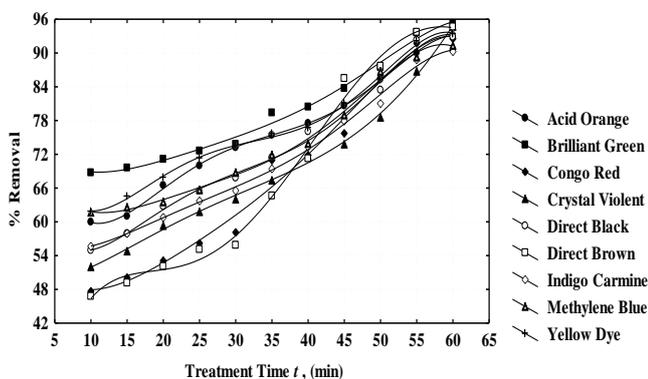


Figure 6. Effect of treatment time (t) on the percent removal of dyes @ $C_o = 1 \text{ mg/l}$, $T_f=45^\circ\text{C}$, pH=1 or 8, $l = 1 \text{ m}$, and $F=5 \text{ ml/min}$

The percentage removal of dyes was increased with decreasing flow rate of SSAS, and initial concentration of dyes while the percentage removal was decreased with increasing of pH, treatment time and the height of adsorbent material PP.

It can be utilized from the residual samples of eggplant peel that adsorb dyes from SSAS as a rodenticide for rodent control.

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