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ISOTHERM AND KINETIC STUDY OF THE ADSORPTION OF DIFFERENT DYES FROM AQUEOUS SOLUTION USING BANANA PEEL BY TWO DIFFERENT METHODS

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ABSTRACT

This work deals with the removal of many dyes from simulated aqueous solution by banana peel (BP). The adsorption processes of nine types of textile dyes: acid orange, brilliant green, Congo red, crystal violent, direct black, direct brown, indigo carmine, methylene blue, and yellow dye were studied. The effects of initial dye concentration, pH, flow rate, media column height, and contact time have been studied at different temperatures. Different Kinetic studies and isotherm models were carried out to observe the effects of various process parameters. Models results show that experimental data have been fitted to Pseudo-second order and Langmuir equation better than other kinetic and isotherm models. The higher removal efficiencies of (89.37, 87.58, 84.52, 92.57, 90.32, 92.67, 89.45, 88.89 and 92.99) % for nine dyes respectively were observed in this study. In another hand, fresh BP was used as a source to extract Polyphenol Oxidase (PPO) which is loaded on the biocatalyst (zeolite type Y) prepared from rice husk and tested in the removal process of the same dyes at high concentrations. The prepared biocatalyst has high removal efficiency (up to 99.12%) of dyes for initial concentration 50 mg/l. The results showed the ability of prepared biocatalyst to remove the dyes at high concentrations.

KEYWORDS: banana peel; dyes; aqueous solutions; PPO; adsorption.

INTRODUCTION

Many industries, such as textiles, pulp mills, leather, printing, food, and plastics, are using dyes in their processes in order to color their products. This dyeing process usually uses both organic and inorganic synthetic dyes which are present in a variety of colors. As a result, a large amount of highly colored effluent was released in their wastewater. Colored wastewater released into ecosystems is a dramatic source of esthetic pollution and perturbation in the aquatic ecosystems by its impending penetration of light as well as food web (Daneshvar *et al*., 2007; Ong *et al*., 2007). Many dyes and their breakdown products may be toxic, carcinogenic and teratogenic for living organisms (Sarioglu & Atay, 2006). In addition, dye wastewaters are commonly characterized by high salt content and low biodegradation potential (Alinsafi *et al*., 2005). Last but not least, wastewater containing dyes is very hard to be treated since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and stable to light, heat and oxidizing agents (Kyzas *et al*., 2012). Due to their inert properties and the low concentration of dye molecules in wastewater, waste water containing dyes are difficult to be removed by conventional treatment processes (Ngah *et al*., 2011). The high cost to remove trace amounts of impurities causes the conventional methods of removing dyes become unfavorable to be applied at a large scale (Crini & Badot, 2008). There are many physical, chemical and biological methods and processes have been employed for the removal of dyes from wastewaters. Numerous approaches have been developed to remove these compounds from colored effluents including biological treatment (Álvarez *et al*., 2013), coagulation/flocculation (Liang *et al*., 2014), reverse osmosis (Al-Bastaki, 2004), ozone treatment (Zhao *et al*., 2006), oxidation (Sharma & Das, 2012), membrane filtration (Zhu *et al*., 2013), photocatalytic degradation (Tayade *et al*., 2009) , ion exchange (Labanda *et al*., 2011), electrochemical techniques (Raghu & Basha, 2007) and adsorption (Vasques *et al*., 2014). Amongst the numerous techniques of dye removal, the adsorption process is one of the effective processes that have been successfully employed for color removal from the wastewater (Doğan *et al*., 2009). The main benefits of this process are the low initial cost, flexibility, and simplicity of design, ease of operation and insensitivity to toxic pollutants. It also does not result in the formation of secondary harmful substances. Various adsorbents like zeolites, polymeric resins, bentonite, peat, ion exchangers and activated carbon have been used for removing colored effluents from aqueous solutions in textile industrial wastewaters (dos Santos *et al*., 2007). Among them, activated carbon is the most widely used to remove pollutants from dye wastewater. However, there still exists the main drawback of high cost and difficult procurement for this adsorbent. Therefore, the development of efficient, low-cost and environmentally friendly adsorbents to reduce dye content in wastewater becomes urgent. In recent years, a number of nonconventional adsorbents have been proposed as an adsorbent for various types of dyes from aqueous solutions, such as rice husk (Lakshmi *et al*., 2009), sugarcane bagasse (Filho *et al*., 2007), fly ash (Mane *et al*., 2007), sludge ash (Weng & Pan, 2006), bituminous coal (Mohan *et al*., 2002), maize cob (Kadirvelu *et al*., 2003), coconut shell (Kannan & Sundaram, 2001), wheat straw (Gong *et al*., 2008), orange peel (AbdurRahman *et al*., 2013), de-oiled soya (Mittal *et al*., 2005), agro-industry waste, mangosteen peel (Ahmad & Alrozi, 2010), rambutan peel (Ahmad & Alrozi, 2011), rubber seed coat (Hameed & Daud, 2008).

Banana is one of the most consumed fruits in the world and there is no industrial use for its peel, so it constitutes a major agricultural waste in different regions of the planet (Ertugay & Bayhan, 2010). Banana peels are readily available, low cost and cheap and environment-friendly bio-materials. The aim of this paper is to test the ability to use banana peel wastes in two ways as adsorbent material in the removal of various dyes: acid orange, brilliant green, Congo red, crystal violent, direct black, direct brown, indigo carmine, methylene blue, and yellow dye from aqueous solutions. The first method is conventional adsorption of dyes using originally banana peel and the second is removing the same types of dyes using extracted Poly Phenol oxidase enzyme from the mature banana peel. The effects of initial dye concentration, solution temperature, pH and repeated desorption–adsorption studies on dye adsorption onto banana peel were investigated. Kinetics, isotherms and thermodynamic parameters governing the adsorption process were also determined and discussed.

MATERIALS & METHODS

Banana peel (adsorbent media)

The authors collected the banana peel (BP) used in this study from local markets in Baghdad city. To remove dust and any other dirt, raw waste material (BP) was washed many times with clean water. Then dry it for 24h at 50°C after cutting it to small sizes (0.5-1 cm).

Preparation of simulated wastewater

The experimental work in this study was conducted by using simulated synthetic aqueous solution of different dyes to prevent any interference with other elements in actual wastewater. Simulated dyes solutions were prepared by dissolved known weight of dyes in 1L distilled water to get 1000 mg/L concentration. After that when need any other concentration was prepared by diluting the stock solution. By using spectrophotometer thermo – genesys 10 UV, USA the dyes concentrations were measured.

Adsorption experimental setup and procedures

To remove the nine dyes from simulated solutions, the continuous mode of fixed bed column was used. Different parameters (dyes concentrations, media heights, flow rate, and pH) were checked by using sorption unit illustrated in Fig.1. The sorption unit consists of glass column (2.54 cm internal diameter and 150 cm height) and two (1 L) glass containers (one for a simulated solution and other for treated solution). After packed the column with desire amount of adsorbent media and before using simulated solutions, it was rinsed with double distilled water. Then, the experiment was started by using of simulated dyes solutions (with desired concentrations, pH, contact times, and temperatures) to flow through the column by gravity from up to down. At regular intervals, filtered samples were withdrawn and analyzed. Dyes concentrations (1-100 mg/l), contact time (10-60 min), temperature (5-45°C), flow rate (5-100 ml/min) and pH (1-8) were optimized by continuous variation method (studying one, while keeping the other parameters constant).

To determine the amount and percentage of dyes removed by the adsorbent, Eqs. 1 and 2 were used.

$$q = \frac{V}{w}\,(C_\circ - C_t) \tag{1}$$

$$R\,(\%) = \frac{(C_\circ - C_t)}{C_\circ} \times 100 \tag{2}$$

Where q is the amount of dye adsorbed onto BP ((mg/g));
$C_\circ$ is the initial concentration of dye (mg/L) at $t = 0$;
C_t is the concentration of dye at $t = t$ (mg/L);
V is the initial solution volume (L);
w is the BP weight (g); and
R is the percentage removal of dye using BP.

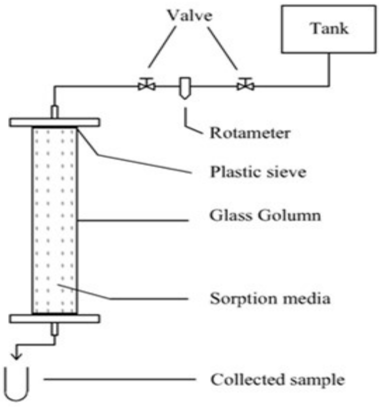

FIGURE 1. Schematic diagram of the adsorption unit

Preparation of crude PPO enzyme extract from BP

Fresh banana peel was used to extract crude poly phenol oxidase (PPO), by following a procedure described in details by Kaviya *et al*. (Kaviya. R *et al*., 2012).

Enzyme assay

To prepare assay solution, 1 ml of 0.2M sodium phosphate buffer, 1 ml of 20 mM substrate (L-DOPA), 0.1 ml of enzyme solution, and 0.9 ml of water were mixing. By using spectrophotometrically at 475 nm, the enzyme activity was measured. One unit of this activity means the amount of enzyme that transforms 1 µmole of substrate per minute under assay conditions (Kaviya. R *et al*., 2012).

Adsorption kinetic model

The mechanism of adsorption onto an adsorbent can be described by several mathematical models. The parameters found in these expressions are important in water and wastewater treatment process design.

The kinetics of dyes adsorption was analyzed using different kinetic models which were the pseudo first order, the pseudo second order, the simple Elovich model and the Intraparticle diffusion model, and as follows (Abbas & Abbas, 2014):

Pseudo-first order kinetic model:

$$\mathrm{Ln}(q_e - q_t) = \mathrm{Ln}\, q_e - k_1 t \qquad (3)$$

Pseudo-second order kinetic model:

$$\frac{dq_t}{d_t} = k(q_e - q_1)^2 \qquad (4)$$

Where q_t (mg/g) is the adsorbed amount at time t, k_1(1/min) and k (mg/(gm·min) are the pseudo-first and second-order rate constant respectively and q_e (mg/gm) is the adsorbed amount at equilibrium. Integrating (4) for the boundary condition t = 0 to t = t and q_t =0 to q_t = q_t, it was rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \qquad (5)$$

Weber–Morriss model: it is expressed by using the intra-particle diffusion model to estimate the rate limiting step of any adsorption process, as follows:

$$q_t = k_i(t)^{0.5} + C \qquad (6)$$

where q_t is the quantity of adsorbed material at any time (mg/gm), K_i is the intra-particle diffusion rate constant, t is the time of diffusion (min) and C is the slope that represents the thickness of the boundary layer.

Adsorption isotherms

In general, the adsorption process is often evaluated by conducting the adsorption isotherms. The Langmuir, Freundlich, BET, Temkin and Dubinin-Radushkevich models are the most extremely used to describe the adsorption isotherms from experimental data. These models provide information to find the removal efficiency of many types of dyes and an estimation of adsorbent amounts needed to remove dyes from aqueous solution. Their mathematical expressions are listed in Table 1 below (Abbas & Abbas, 2014).

TABLE 1. The mathematical expressions of adsorption isotherm models

Model	Original form	Linearized form
Langmuir	$q = \frac{q_m . K_L . C}{1 + K_L . C}$	$\frac{C}{q} = \frac{1}{q_m . K_L} + \frac{C}{q_m}$
Freundlich	$q = K_F . C^{\frac{1}{n}}$	$\log q = \log K_F + \frac{1}{n} \log C$
BET	$q = \frac{K_B . C . q_m}{(C_s - C)[1 + (K_B - 1)\left(\frac{C}{C_s}\right)]}$	$\frac{C}{q(C_s - C)} = \left(\frac{1}{K_B . q_m}\right) + \left(\frac{K_B - 1}{K_B . q_m}\right) . \left(\frac{C}{C_s}\right)$
Temkin	$q = \frac{\mathbb{R} T}{b_T} \ln(A_T C)$	$q = \frac{\mathbb{R} T}{b_T} \ln A_T + \frac{\mathbb{R} T}{b_T} \ln C$
Dubinin-Radushkevich	$q = q_s . \exp(-k_{DR} \varepsilon^2)$	$\ln q = \ln q_s - k_{DR} \varepsilon^2$

Where:

q The adsorbed amount per adsorbent amount (mL/g).

q_m The adsorbed amount required to form a monolayer.

n The Freundlich equilibrium constant that related to the intensity of adsorption.

C The concentration of adsorbed substance (mL/L).

C_s The concentration of solute at the saturation of all layers (mL/L).

K_L The Langmuir equilibrium constant (L/ mg).

K_F The Freundlich equilibrium constant that related to the total adsorption capacity (mg/g).

K_B The BET constant.

$\mathbb{R}$ The universal gas constant = 8.314 $\frac{J}{mol.\ K}$

A_T The Temkin isotherm equilibrium binding constant (L /g).

b_T The Temkin isotherm constant.

q_s The theoretical isotherm saturation capacity (mg/g).

k_{DR} The Dubinin–Radushkevich isotherm constant (mol^2/ kJ^2).

ε The Dubinin–Radushkevich isotherm constant (potential energy).

$$\varepsilon = R\, T \ln\left(1 + \frac{1}{C_e}\right) \qquad (7)$$

In Dubinin-Radushkevich model the approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship:

$$E = \frac{1}{\sqrt{2\beta}} \qquad (8)$$

Where β is denoted as the isotherm constant.

From the Langmuir equation, a further analysis can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor. It is given by the expression:

$$R_L = \frac{1}{1+K_L.C} \tag{9}$$

The value of R_L lies between 0 and 1 for favourable adsorption, $R_L > 1$ represents unfavourable adsorption, $R_L = 1$ represents linear adsorption and the adsorption process is irreversible if $R_L = 0$.

RESULTS AND DISCUSSION

Effect of initial concentration

Fig. 2 shows the effect of dyes initial concentration (C_o) on removal percentage. For all nine dyes, as shown in this figure, the percentage removal of dyes was decreased when the initial concentration (C_o) was increased with other variables held constant. To explain this we must know that the adsorbent media had a limit number of active sites which saturated with a certain amount of dyes. When increased dyes initial concentrations with fixed amount of media that leads to increasing dyes molecules compared to limited media sites, which lead to flow out excessive dyes. These results are consistent with that of previous studies (de Carvalho *et al.*, 2015). So, the relation between initial concentration and removal percent was inverse. Higher removals efficiencies were (89.37, 87.58, 84.52, 92.57, 90.32, 92.67, 89.45, 88.89 and 92.99) % for nine dyes respectively at initial dye concentration of 1 mg/l. The results of this parameter showed that the adsorbent media was efficient to remove dyes from solutions.

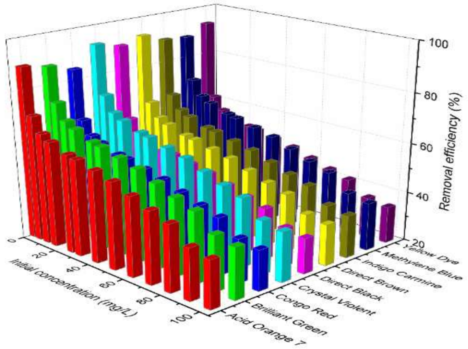

FIGURE 2. Effect of initial concentration on the removal efficiency

Effect of pH

The nine dyes, according to pH's effect (as shown in Fig. 3a-b), can be classified into two groups. The percentage removal of the first group (acid orange, Congo red, direct black, direct brown and indigo carmine) decreased when simulated solution pH was increased with other variables held constant(Fig. 3a). While, the percentage of the second group (crystal violent methylene blue, brilliant green, and yellow dye) increased when pH was increased with other variables held constant (Fig. 3b).

The pH, as is known, is an important parameter in affecting the adsorption of dyes, since it can affect at the same time the ionization degree of functional groups of the adsorbate, the surface charge of the adsorbent, in addition to the mechanism of adsorption. The increasing in percentage removal of the first group at low pH can be explained as follow. The adsorbent surface, at low pH, was become highly protonated and it will be suitable for adsorption of first group dyes. The degree of protonation of the BP surface reduced with increased in pH, hereafter adsorption is decreased. When pH increases, additionally, it will happen a competition between hydroxide ion (OH^-) and first group dyes, which led to limited in net positive surface potential of sorbent media, resulting in a minimizing of the electrostatic attraction between the dyes and BP surface. So, all above reasons led to reducing sorption capacity which ultimately caused decreasing in percentage adsorption.

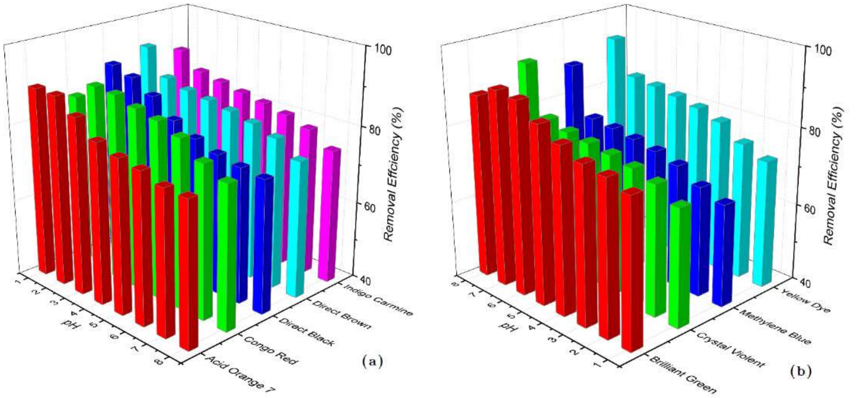

FIGURE 3. Effect of pH on the removal efficiency

While, for the second group adsorption processes, it could be explained by ion-exchange mechanism, when the important role is played by functional groups that have cation exchange properties. Due to competition between hydrogen and dyes molecules on sorption sites, in this case, and at low pH, dyes removal was inhibited. But, when the pH increased, this will led to increasing in the negative charges density on the adsorbent surface. The attraction of dyes molecules to sorbent materials, which had positive charges, was increased, finally, the adsorption percentage will be increased, same observations were considered by other researchers (Abbas, 2013; Elmoubarki *et al*., 2015).

Effect of adsorbent media bed height

When the adsorbent media height was increased, as shown in Fig. 4, removal percentage was increased too. This occurred because of, the additional amount of adsorbent media meaning increasing in the surface area available, then the active sites increased also, which gave high removal percent of dyes (Fig. 4), a similar result was also observed in the recently conducted study(Ali *et al*., 2016).

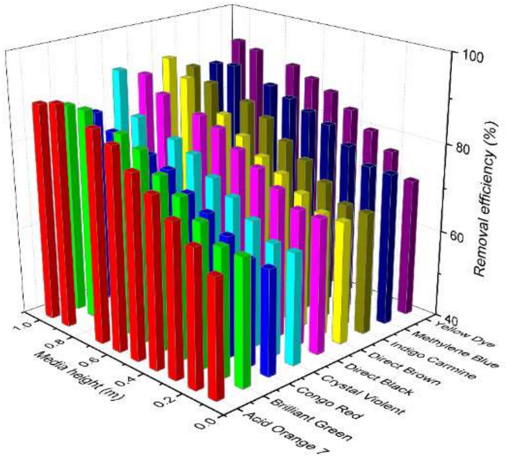

FIGURE 4. Effect of adsorbent media height on the removal efficiency

Effect of flow rate

The effect of simulated solution flow rate on dyes removal percentage was shown in Fig. 5, it is clear that when the flow rate was increased, the percentage removal of dyes was decreased with other variables held constant. This may be due to the fact that when the flow rate increased, the velocity of the solution in the media was increased too, so the solution spends shorter time than that spends in the column while at low flow rate, which means little contact time between dyes and media (Fig. 5).

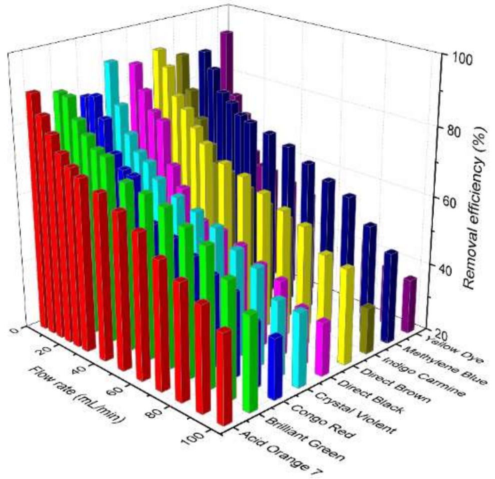

FIGURE 5. Effect of SASS flow rate on the removal efficiency

Effect of feed temperature

Evaluation of temperature was carried out with the range of 5 to 45°C for testing the ability of BP in dyes removal. Fig. 6 shows that when the temperature of feed (simulated solution of dyes) was increased, the percentage removal of dyes was increased too with other variables held constant. In addition, increasing the temperatures may occur some structural changes in the dyes and the adsorbent during the adsorption, these changes resulting in good effects enabling dyes ions to adsorb further (as shown in Fig. 6).

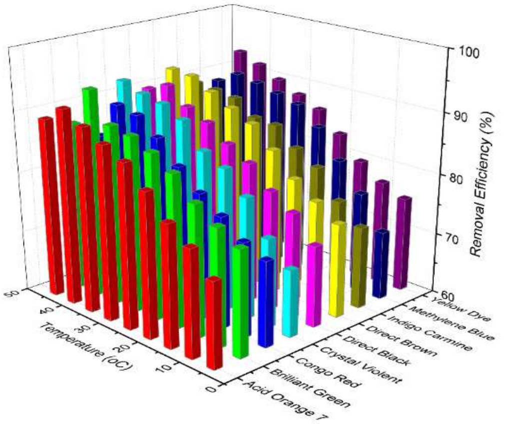

FIGURE 6. Effect of SASS temperature on the removal efficiency

Effect of contact time

The effect of contact time on dyes removal by BP is explained in Fig. 7. The adsorption process was conducted for several times (10-60 min). The dyes removal efficiency increased when contact time was increased (Fig. 7). This may be due to the fact that under higher contact time, the higher interaction between the sorbent surface and dyes (Ali *et al*., 2016).

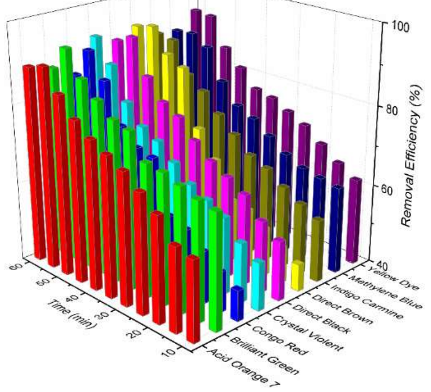

FIGURE 7. Effect of treatment duration on the removal efficiency

Statistical model

To analyze the results obtained from this experimental work, a statistical modelling was used. To find the relation between the percentage removal of dyes and operational parameters (temperature, flow rate, pH, the initial concentration, adsorbent media (BP) height, contact time, column diameter and other parameters), regression analysis and $\boldsymbol{\pi}$ theorem were adopted. Results of these relations were shown in Table 2, which explained high efficiencies, as can be seen in R^2 column (0.993-0.998).

TABLE 2. Statistical equations of dyes removal using banana peel

Dye	Equation	R^2
Acid Orange	$\%R = 5.201 \times 10^{-6}\left(\frac{\rho_{sol}}{C_\circ}\right)^{0.2181}.\left(\frac{l}{d}\right)^{0.2055}.\left(\frac{T_f.C_{P_{sol}}.t}{\vartheta}\right)^{0.0578}.\left(\frac{K_{sol}.T_f}{\gamma.u}\right)^{0.2688}.\left(\frac{1}{pH}\right)^{0.0082}$	0.998
Brilliant Green	$\%R = 3.816 \times 10^{-6}\left(\frac{\rho_{sol}}{C_\circ}\right)^{0.2054}.\left(\frac{l}{d}\right)^{0.2103}.\left(\frac{T_f.C_{P_{sol}}.t}{\vartheta}\right)^{0.0172}.\left(\frac{K_{sol}.T_f}{\gamma.u}\right)^{0.2240}.(pH)^{0.0719}$	0.993
Congo Red	$\%R = 3.779 \times 10^{-6}\left(\frac{\rho_{sol}}{C_\circ}\right)^{0.2199}.\left(\frac{l}{d}\right)^{0.2528}.\left(\frac{T_f.C_{P_{sol}}.t}{\vartheta}\right)^{0.0025}.\left(\frac{K_{sol}.T_f}{\gamma.u}\right)^{0.2007}.\left(\frac{1}{pH}\right)^{0.0012}$	0.994
Crystal Violent	$\%R = 2.255 \times 10^{-6}\left(\frac{\rho_{sol}}{C_\circ}\right)^{0.2539}.\left(\frac{l}{d}\right)^{0.2444}.\left(\frac{T_f.C_{P_{sol}}.t}{\vartheta}\right)^{0.0185}.\left(\frac{K_{sol}.T_f}{\gamma.u}\right)^{0.1905}.(pH)^{0.0331}$	0.994

Direct Black	$\%R = 4.412 \times 10^{-6} \left(\frac{\rho_{sol}}{C_{\circ}}\right)^{0.2493} . \left(\frac{l}{d}\right)^{0.2531} . \left(\frac{T_f . C_{P_{sol}} . t}{\vartheta}\right)^{0.0974} . \left(\frac{K_{sol} . T_f}{\gamma . u}\right)^{0.2107} . \left(\frac{1}{pH}\right)^{0.0606}$	0.997
Direct Brown	$\%R = 3.566 \times 10^{-6} \left(\frac{\rho_{sol}}{C_{\circ}}\right)^{0.1887} . \left(\frac{l}{d}\right)^{0.2643} . \left(\frac{T_f . C_{P_{sol}} . t}{\vartheta}\right)^{0.0982} . \left(\frac{K_{sol} . T_f}{\gamma . u}\right)^{0.1369} . \left(\frac{1}{pH}\right)^{0.0017}$	0.998
Indigo Carmine	$\%R = 5.315 \times 10^{-6} \left(\frac{\rho_{sol}}{C_{\circ}}\right)^{0.2271} . \left(\frac{l}{d}\right)^{0.1955} . \left(\frac{T_f . C_{P_{sol}} . t}{\vartheta}\right)^{0.0715} . \left(\frac{K_{sol} . T_f}{\gamma . u}\right)^{0.0997} . \left(\frac{1}{pH}\right)^{0.0251}$	0.994
Methylene Blue	$\%R = 2.025 \times 10^{-6} \left(\frac{\rho_{sol}}{C_{\circ}}\right)^{0.2076} . \left(\frac{l}{d}\right)^{0.2711} . \left(\frac{T_f . C_{P_{sol}} . t}{\vartheta}\right)^{0.2285} . \left(\frac{K_{sol} . T_f}{\gamma . u}\right)^{0.1007} . (pH)^{0.0059}$	0.997
Yellow Dye	$\%R = 5.986 \times 10^{-6} \left(\frac{\rho_{sol}}{C_{\circ}}\right)^{0.2669} . \left(\frac{l}{d}\right)^{0.1869} . \left(\frac{T_f . C_{P_{sol}} . t}{\vartheta}\right)^{0.1942} . \left(\frac{K_{sol} . T_f}{\gamma . u}\right)^{0.0415} . (pH)^{0.0075}$	0.996

where:

$\%R$	Percent Removal of Cerium from SSAS
ρ_{sol}	Density of SSAS, (kg/m^3)
$C_{\circ}$	Initial Concentration of Cerium , (kg/m^3)
l	Adsorbent Material Bed Height, (m)
d	Internal Diameter of Sorption Column, (m)
T_f	Feed Temperature, (K)
$C_{P_{sol}}$	Heat Capacity of SSAS, (kJ/kg. K)
t	Treatment Time, (s)
ϑ	kinematic viscosity of SSAS, (m^2/s)
K_{sol}	Thermal Conductivity of SSAS , (W/m. K)
σ	Surface Tension, (N/m)

Kinetic study

In order to determine the sorption kinetic models of the different type of dyes, the pseudo first order, the pseudo second order and the Intraparticle diffusion models were applied to the obtained data from experimental work. The calculations were conducted for optimum operation conditions to find the best kinetic model. The adsorption kinetic parameters and correlation coefficients of these models were determined and listed in Table 3.

TABLE 3. Values of the pseudo first order, the pseudo second order, the simple Elovich model and the Intraparticle diffusion constants at optimum operation conditions (C_o = 1 mg.l^{-1}, pH = 8 or 1, l = 1 m, F = 5 ml.min^{-1}, and T_{feed} = 45 °C)

Dye	Pseudo first-order			Pseudo second-order			Intraparticle diffusion		
	q_e	k_1	R^2	q_e	k_2	R^2	k_i	I	R^2
Acid Orange 7	51.47	0.055	0.86	46.83	0.026	0.99	3.11	1.56	0.89
Brilliant Green	39.61	0.003	0.84	42.78	0.020	0.99	3.00	2.03	0.85
Congo Red	45.71	0.035	0.93	48.13	0.021	0.99	3.71	0.81	0.83
Crystal Violent	41.00	0.017	0.83	40.06	0.028	0.99	3.54	2.58	0.82
Direct Black	42.55	0.032	0.95	48.97	0.024	0.99	3.96	1.75	0.90
Direct Brown	53.70	0.003	0.80	43.31	0.026	0.99	3.35	0.84	0.80
Indigo Carmine	41.83	0.018	0.90	48.80	0.023	0.99	2.98	2.06	0.86
Methylene Blue	45.17	0.030	0.89	41.03	0.021	0.99	3.14	3.01	0.83
Yellow Dye	50.52	0.009	0.89	47.96	0.026	0.99	2.99	2.40	0.87

As clear from this table the kinetic data were better fitted by the pseudo second order model than by the pseudo first order model. The pseudo second order model indicates that chemisorption dominated in the adsorption process (Vimonses *et al*., 2009). The difference in the adsorbed concentration of adsorbate at equilibrium (qe) and at time t (qt) is the key driving force for the adsorption, and the adsorption capacity is proportional to the number of active adsorption sites occupied on the adsorbent (Shen *et al*., 2009; Wang *et al*., 2011).

To reveal the relative contribution of surface and intraparticle diffusion to the kinetic process, the kinetic adsorption data were further fitted with the Weber–Morris model. This kinetic model was expressed using the intra-particle diffusion model to estimate the rate limiting step of any adsorption process. According to this model, the plot of uptake (q_t) versus the square root of time ($t^{½}$)

should be linear if intraparticle diffusion is involved in the adsorption process (Arami *et al.*, 2008). As can be seen from Table 3, the removal of dyes by BP involves two stages by surface sorption and intraparticle diffusion. The first one can be attributed to external surface adsorption or an instantaneous adsorption stage, where the dye molecules are transported to the external surface through film diffusion and its rate is very fast. The second region is due to a gradual adsorption stage, where the mercury molecules are entered into bentonite particle by intraparticle diffusion (Kumar *et al.*, 2005). The correlation coefficients R^2 values indicate that the pseudo-second-order model is the most

Adsorption isotherms

The Langmuir, Freundlich, BET, Temkin and Dubinin–Radushkevich were used to describe the data derived from the adsorption experiments. The isotherm constants according to equations listed in Table 1 were calculated and presented in Table 4.

It is noted from this table that the applicability of the simple Langmuir equation for the present isotherm data indicates that the Langmuir equation was able to describe properly the isotherm of removal dyes on BP. A Langmuir isotherm model shows better fitting (R^2= 0.99) with the experimental data compared to another isotherm models. This indicates the applicability of monolayer coverage of dyes on the homogeneous surface of the adsorbent.

TABLE 4. Values of Langmuir, Freundlich, BET, Temkin and Dubinin–Radushkevich isotherm constants for the adsorption of dyes on banana peels at optimum conditions (C_o = 1 mg.l^{-1}, pH = 8 or 1, l = 1 m, F = 5 ml.min^{-1}, and T_{feed} = 45 °C)

Dye	Parameter	Acid Orange 7	Brilliant Green	Congo Red	Crystal Violent	Direct Black	Direct Brown	Indigo Carmine	Methylene Blue	Yellow Dye
Langmuir Isotherm Model	q_m	12.05	22.443	18.627	21.21	19.341	15.621	18.918	11.026	19.55
	K_L	0.235	0.542	0.729	0.621	0.709	0.507	0.720	0.420	0.252
	R_L	0.169	0.583	0.382	0.332	0.482	0.512	0.295	0.425	0.507
	R^2	0.99	0.994	0.994	0.999	0.999	0.994	0.994	0.995	0.996
Dubinin-Radushkevich Isotherm Model	qs	15.05	13.62	11.52	14.72	17.63	9.50	12.63	10.72	11.73
	$k_{DR} \times 10^{-6}$	1.002	3.15	2.035	1.44	2.207	0.983	2.076	1.179	1.85
	E	0.41	2.18	0.98	1.63	1.42	1.50	0.85	2.06	1.64
	R^2	0.79	0.72	0.78	0.75	0.72	0.75	0.72	0.77	0.73
Freundlich Isotherm Model	K_f	5.316	7.603	6.511	4.06	5.819	5.028	8.013	7.118	4.783
	n	1.281	1.728	1.644	1.10	1.562	1.338	1.483	1.720	1.602
	R^2	0.89	0.85	0.87	0.84	0.78	0.75	0.81	0.79	0.75
BET Isotherm Model	q_m	0.82	3.09	0.94	2.04	1.52	3.95	0.88	2.52	1.0
	K_B	3.26	4.32	7.52	1.52	2.05	1.38	5.0	2.28	6.17
	R^2	0.73	0.64	0.74	0.66	0.69	0.78	0.71	0.64	0.75
Temkin Isotherm Model	A_T	9.351	7.483	6.321	9.01	8.308	5.923	6.729	7.303	7.126
	b_T	64.893	62.107	66.520	61.67	63.253	64.074	65.925	61.038	66.82
	R^2	0.784	0.715	0.754	0.736	0.795	0.724	0.751	0.743	0.737

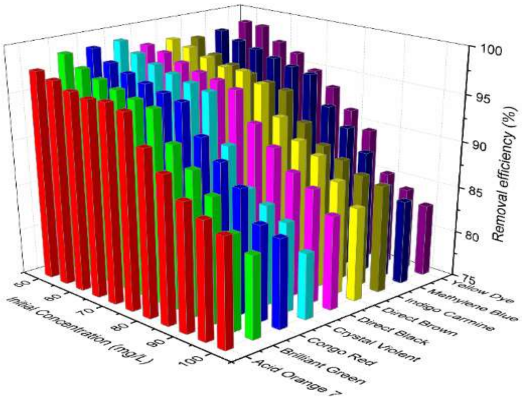

FIGURE 8. Effect of initial concentration ($C_\circ$) on the percent removal dyes using biocatalyst (@ T=25°C, pH=7, and t=60 min)

Application of immobilized PPO (biocatalyst)

By depending on the optimum operation conditions (which were: temperature 25°C, pH 7, flow rate 5ml/min and biocatalyst media height 1m), while the initial concentrations of dyes solutions were varied between (50-100) mg/l, the immobilized PPO (biocatalyst) was tested to remove nine dyes from simulated solutions. This part of the study was conducted by using same sorption unit. The results were shown in Fig. 8, which showed a high removal efficiency of PPO (up to 99.12%) for dyes removal.

PPO (biocatalyst) ability to adsorb dye is mainly due to it is consists of cellulose, pectine, hemicellulose, lignin, low molecular weight hydrocarbons, and hydroxyl groups such as carboxyl and hydroxyl. These components help in removing dye ions from aqueous solutions(Abbas, 2013).

CONCLUSIONS

The biosorption of nine dyes (acid orange, brilliant green, Congo red, crystal violent, direct black, direct brown, indigo carmine, methylene blue, and yellow dye) from simulated solution onto the natural banana peel and PPO (biocatalyst) has been studied. The effects of different operation parameters on removal efficiency were checked. The following conclusions can be drawn from results:

1. Banana peel (BP) acts as a valuable adsorbent for removal of dyes from simulated solution.
2. Brilliant green, crystal violent methylene blue, and yellow dyes' removal efficiencies were increased by increasing pH. While remaining dyes efficiency were decreased with increasing pH.
3. When decreasing of dyes flow rate and initial concentration, it shows increasing in removal percentage.
4. By increasing contact time and BP height led to increasing in removal efficiencies.
5. Maximum removal efficiencies were (89.37, 87.58, 84.52, 92.57, 90.32, 92.67, 89.45, 88.89 and 92.99)% for nine dyes, respectively.
6. By using PPO (biocatalyst), high removal percentages were achieved, especially for high concentrations (between 50-100 mg/l).
7. Finally, by this study, it can possess different benefits which are: remove nine toxic dyes contaminated the water and get rid of agricultural waste BP, i.e. it can discard polluted waste in a cost-effective and eco-friendly method.

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