Egypt. J. Chem. **Vol. 65**, No.5 pp. 23 - 31 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Treatment of Blue HB Reactive Dyes in Textile Wastewater using Bio-waste based Hydroxyapatite

Mona A. Abdel-Fatah*[1], Ehab Abadir[2], Ghada A. Al Bazedi[1]

[a] *Chemical Engineering & Pilot Plant Department, Engineering Research Division, National Research Center, 33 El-Bohouth St., Dokki, Cairo, Egypt, Post Code 12622*

[2]*Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt*

Abstract

Textile industry produces large quantities of wastewater which represent a high health hazard. The main purpose of this research is to investigate and evaluate the ability of using hydroxyapatite as adsorbents in the treatment of textile dye waste near neutral pH values, which gives another benefit of reusing the treated water without further pH adjustment. In the present study, hydroxyapatite from fish scales was used as an adsorbent for HB blue dye. Hydroxyapatite was characterized using SEM, EDX and FTIR. Adsorption kinetics was modeled using both pseudo-first-order model and pseudo-second-order model. Equilibrium isotherm are studied and Langmuir model (i.e. Freundlich, Langmuir, and BET). The Langmuir adsorption model is better describing the adsorption with correlation coefficients for the HB blue dye with R^2 equals 1. To achieve a removal efficiency of 85 % in aqueous solution, the optimum adsorbent dose required is 20 mg.

Keywords: Hydroxyapatite, wastewater, Blue HB dye, Bio-waste

1. Introduction

The existence of dyes in textile effluents is relatively perceived, it affects the characteristics and the clearness of the water in the receiving lines. It additionally reduces the regeneration capacity through the reduction of sunlight penetration affecting the aquatic life biological and chemical activities [1-3].

The excessive diversification and multifariousness of these effluents associated with the employment of environmental laws, which oblige that they endure adequate treatment, have guided to the elaboration of recent technologies that pursue the most appropriate treatment to disintegrate or restrain toxic organic compounds, bearing in mind the costs of treatment, time and adeptness of the processes in treating and reusing of industrial water [3, 4].

Wastewater contagion with detrimental dyes is a critical relies in cutting-edge industrial circles because of its low degradability, excessive toxicity, and high stability to photo degradation. Blue dyes are a typical example of an industrially significant toxic cationic dye with harmful effects on humans, as it is extensively used in textile dying [5-7].

Releasing of colored dyes despite miniscule amounts into water streams deprived of proper treatments might produce water with an in auspicious coloration and an intense increase in the chemical oxygen demand and toxicity, especially when these dyes break down into carcinogenic materials. Roughly estimated the number of existing commercial synthetic dyes and pigments exceeds 10000 with a production capacity moving toward 7×105 tons/year. The aromatic nature of synthetic dyes (highly water soluble), especially, conjures up a dangerous effect to aquatic animals and vegetation; necessitating a proper remediation for those effluents before discharging into water bodies [8].

In this regard, various biological, chemical and physical procedures have been applied for dyes removal in wastewater treatment. Biological methods

*Corresponding author e-mail: monaamin46@gmail.com; (Mona A. Abdel-Fatah).
Receive Date: 09 January 2022, Revise Date: 17 January 2022, Accept Date: 18 January 2022
DOI: 10.21608/EJCHEM.2022.115407.5234

including aerobic or anaerobic treatment cause biodegradation of dyes. However, since biological treatment is depended on climate change and reactor's size, this type of treatment is not appropriate for large capacities as it shows low dyes' removal efficiency.

Alternatively, coagulation/flocculation of dyes with chemical agents produces big contaminated sludge requiring special treatment. Another alternative, the physical treatments covered filtration, reverse osmosis and adsorption which exhibited an advanced dyes' removal performance at reasonable cost and easy processing. The adsorption technique shows low sensitivity to toxic materials; keeping off the complications associating membrane-based technologies [9, 10].

Attracting sorbents including natural and modified clay, chitosan, zeolites, fly ash, coal, paper mill sludge and agricultural/industrial wastes as surrogates for the conventional materials. The hydroxyapatites are known for their genuine ability to retain various metals, due to their surface characteristics. Hydroxyapatite (Hap) is a bio-ceramic material that has been produced for applications in orthopedic applications [10-14]. However, usage in environmental biotechnology fields is increasingly gaining the attention of many researchers, mainly for elimination of fluorides as well as the removal of heavy metals. Remarkably, the sorption of Pb by Hap has been significantly studied by researchers [12-15].

Different researchers have investigated the availability of hydroxyapatite to treat dye containing wastewater. W. Lemlikchi et al. (2011) explored the treatment of textile wastewater using both hydroxyapatite and with regenerated hydroxyapatite. The results indicate the potential use of regenerated hydroxyapatite with high adsorption capacity [16]. Also W. Lemlikchi et al. (2015), studied the kinetics of adsorption of different dyes in aqueous solution on hydroxyapatite. The results showed that the equilibrium data fit well to the Freundlich isotherm [17].

The adsorption of hydrant blue dye on hydroxyapatite at neutral and basic pH value was investigated by Noura Oubagha et al. (2017), the results imply that the co-precipitation mode is not obtained at the higher dye concentration (500 mg/L), and only 10% removal efficiency is observed for a dye concentration of higher values (1 g/L) [18]. Chitosan combined with hydroxyapatite was investigated by Ragab Ahmed et al. (2019) for the treatment of brilliant green dye (BG) from a solution. The structure and morphology of the prepared material was studied by "FTIR, XRD, SEM and TEM". By studying the equilibrium, it was found to follow the Dubinin–Radushkevich isotherm model indicating that sorption was governed by physical-chemical adsorption [19].

The aim of this research is to investigate and evaluate the possibility of using hydroxyapatite as an adsorbent in the treatment of textile dye waste. On the other hand, applying water treatment using hydroxyapatite near neutral pH value, which gives another benefit facilitating the treated water to revert to the environment deprived of pH adjustment.

2. Material and Techniques

3. Materials

The details of the materials used in this paper, such as (hydroxyapatite, dye, and wastewater) are as follows:

2.1.1 Hydroxyapatite preparation

Tilapia scales were collected from the fish market, Cairo-Egypt. The scales were first washed for several times in running water. The scales are then immersed in 0.1M/L HCl solution, and then washed using distilled water. Subsequently, the scales are dried in an oven at 80°C for 24-hr, then crushed to small size. The sieved material was washed several times in distilled water and then dried again in an oven at 80°C for another 24 h. This is to ensure a uniform product for use during the adsorption tests.

2.1.2 Wastewater and Reactive dye

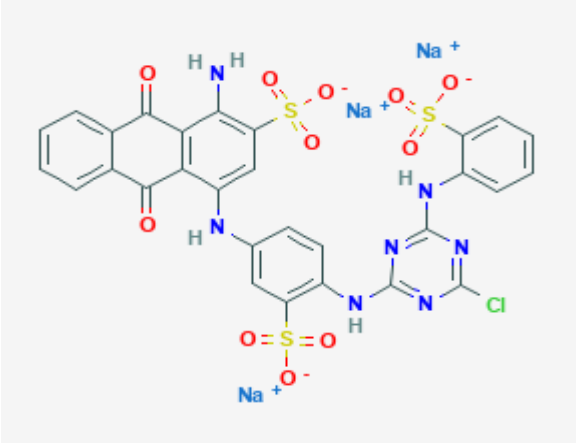
The wastewater effluent and the textile dye characteristics are presented in Tables 1 and 2. All experiments were carried out in air at ambient temperature by mixing about 100 mL of synthetic dye solutions with different concentrations (50-300 mg/l) with the selected HA solution amount, additional pH re-adjusting to 8, with continuous mixing.

Table (1) Wastewater Effluent Characteristics

Parameter	Sample
Dye concentration mg/l	50 - 300
Temp. (°C)	35–45
pH	6–10 (9*)
Colour (Pt–Co)	50–2500
COD (mg/l)	150–12,000 (1279*)
BOD (mg/l)	80–6000
TDS (mg/l)	2900–31000 (10450*)
TSS (mg/l)	15–8000

* used values

Table (2) HB dye Characteristics

Parameter	C.I. Reactive Blue 2
Molecular Formula	$C_{29}H_{17}ClN_7Na_3O_{11}S_3$ 
Molecular Weight	840.1 g/mol
Color	Blue

2.1.3 Techniques

The adsorption kinetics was defined by homogenizing 50 mg of the adsorbent in 20 mL of dye solution (150 mg/L) in the selected pH range from the previous studies. The mixtures were shaken at 25°C, for time intends varying 15 to 360 min. The samples were taken from the solutions at definite time intervals and centrifuged at 10,000 rpm for 5 min. The residual dye concentration was estimated Spectro-photo-metrically using a UV–vis spectrophotometer (Instrutherm A-200) and 1-cm path-length cell for monitoring absorbance at a wave length 592nm. The amount of dye adsorbed by the bio-sorbent in the following mass balance Equation (1):

$$q_t = (C_o - C_t) \times \frac{V}{m} \qquad (1)$$

Where: q_t (mg/g) is "the amount of adsorbed dye per unit weight of specific bio-sorbent at any time t"; C_0 (mg/L) and C_t (mg/L) are respectively "the initial concentrations and the concentrations of time t'; V is "the volume of the dye solution" (L); and m is the "mass of bio-sorbent used" (g).

The adsorption kinetics that describes the solute "uptake rate" at the solid–solution interface, were analyzed by applying "pseudo-first order" equation (2) and |pseudo-second-order" equation (3):

$$\ln(q_e - q_t) = \ln\ q_e - K_1\ t \qquad (2)$$

$$\frac{t}{q_t} - \frac{1}{K_2 \times q_e^2} + \frac{t}{q_e} \qquad (3)$$

Where: q_e (mg/g) and q_t (mg/g) are "the solid phase equilibrium concentration and the amount of dye adsorbed per unit weight of bio-sorbent at any time t", k_1 (hr), k_2 (g/mol.hr) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

Adsorption isotherms were defined from the equilibrium adsorption tests in a "batch reactor" using different concentrations with 100 mL of un-buffered dye solutions. All the experiments were achieved at constant agitating rate of 200 rpm at of c constant temperature (25°C) in a thermostatically controlled outer circulating-water bath. The "Langmuir and Freundlich" models were applied to explain the "adsorption isotherm".

3. Results and Discussions

3.1 Characterization of hydroxyapatite adsorbent

3.1.1 SEM and EDX

The "surface morphology" and the "microstructure" of the hydroxyapatite powder were probed by a "Field Emission Scanning Electron Microscope (SEM) (JEOL: JXA-840A)". The image study and conclude of the chemical composition of the adsorbent were conducted by SEM. Figure (1) shows image of the surfaces at a magnification of "600X" for studied adsorbent. The structure observed through image analysis of the adsorbent samples show irregular surface including cracks and cavities, thus supporting the adsorption mechanism. The chemical composition of the adsorbent is: oxygen (56.46%), aluminum (5.34%), phosphorus (14.07%), and calcium (24.12%).

❑ **Summary of adsorption isotherms**

Name	Isotherm equation	Application	Note
Langmuir	$\theta=\frac{C_s}{C_\infty}=\frac{B_0P}{1+B_0P}$	Chemisorption and physisorption	Useful in analysis of reaction mechanism
Temkin	$\theta=c_1\ln(c_2P)$	Chemisorption	Chemisorption
Freundlich	$\theta=c_1p^{1/C_2}$	Chemisorption and physisorption	Easy to fit adsorption data
BET	$\frac{P/P_0}{V(1-P/P_0)}=\frac{1}{cV_m}+\frac{c-1}{cV_m}(P/P_0)$	Multilayer physisorption	Useful in surface area determination

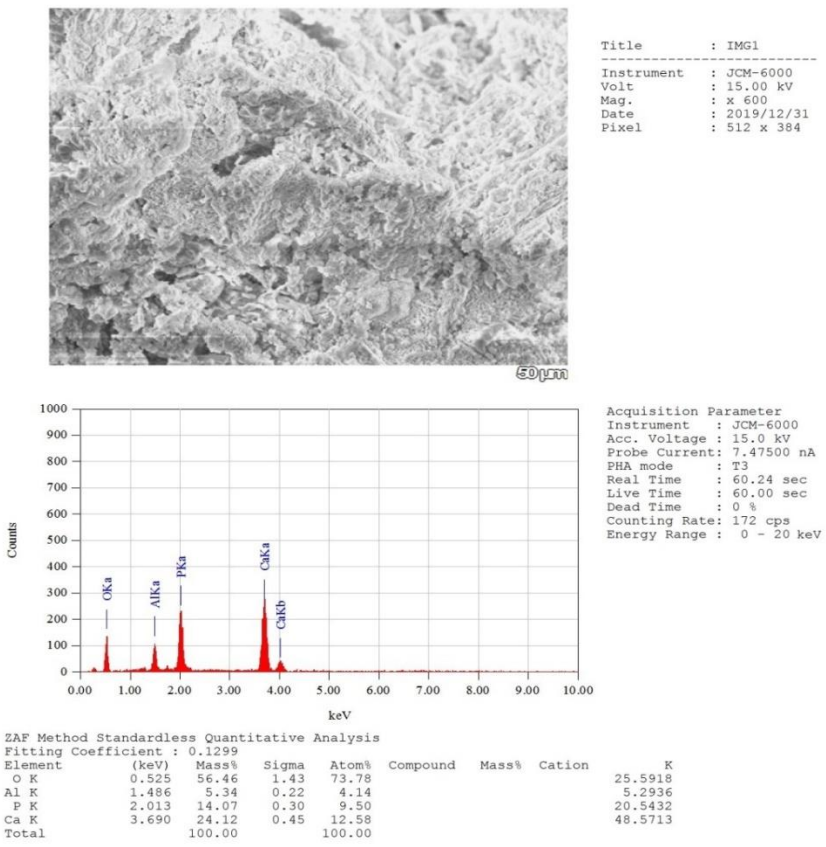


Figure **(1) SEM and EDX analysis of the prepared hydroxyapatite**

The micrograph also displays the roughness of the composite surface with a porous structure, signifying that the prepared adsorbent may have an effective adsorption capacity.

3.1.2 FTIR

An FTIR spectrum of the prepared Hydroxyapatite was determined using "FT/IR-6100 type A Jasco-Japan TGS detector with the absorbance technique wavelength ranging from 500 to 4000 cm^{-1} with scanning speed of 2 mm/s". The detected bands include two bands were observed at 3439 cm^{-1} and 1632 cm^{-1} owing to the stretching mode of "hydrogen-bonded OH^- ions" and liberation mode of "hydrogen-bonded OH^- ions". Another band observed at 1042 cm^{-1} which is accredited to ν3 PO_4, while the bands at 609 cm^{-1} and 553 cm^{-1} were attributed to ν4 PO_4. The "FTIR analysis" illustrated all typical absorption bands of hydroxyapatite. The FTIR results are in agreement with published ones [20-22]. Shown in Figure (2) FTIR of hydroxyapatite

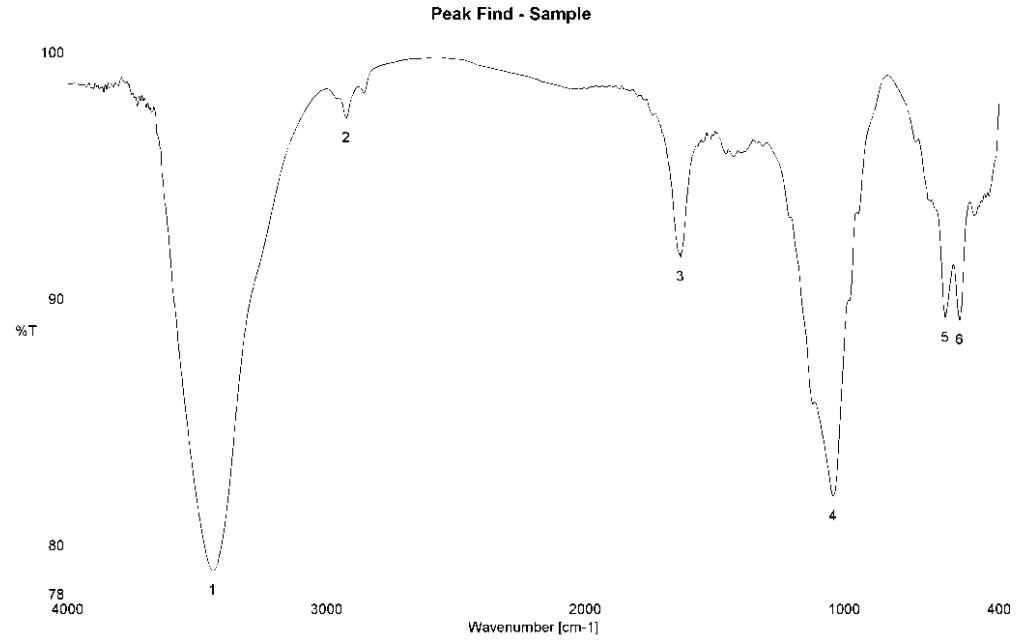


Figure **(2) FTIR spectra of hydroxyapatite**

3.2 Equilibrium Isotherms

The adsorption isotherm Figures (3, 4) show the charts of different isotherm models applied to investigate the equilibrium data achieved in this study. The parameters attained shows that "Langmuir isotherm" model gives the best fit with the R^2=1, the results of the equilibrium study are in agreement with published results for similar types [23-25].

3.2.1 Effect of Initial Adsorbent Dose

The impact of adsorbent dosage on the HB blue dye removal was realized by using various dosages of hydroxyapatite from 5 mg up to 25 mg.

The removal efficiency of different doses is displayed in Figure (5). It was observed that the optimum adsorbent dose for dye removal is at 20 mg where the removal efficiency mounted to 85 %. Nevertheless, excess amount of adsorbent (25 mg) was used, a reduced the adsorption efficiency which may be due to dense packed interlayer that make it harder to adsorb more dye.

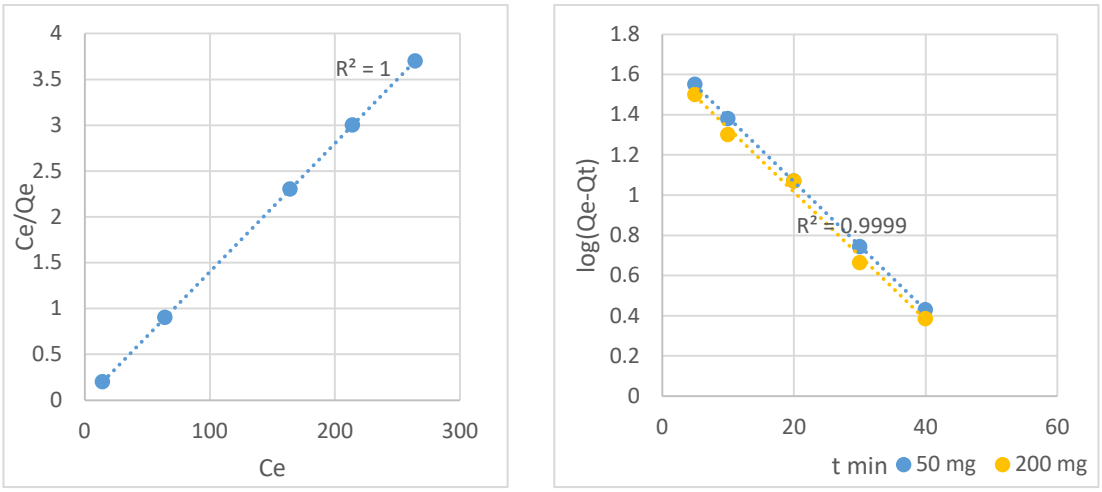


Figure **(3) Pseudo first order kinetics for Blue HB dye removal (**Langmuir isotherm model) (Co: 50 mg/l, adsorbent dose: 5 mg up to 25 mg)

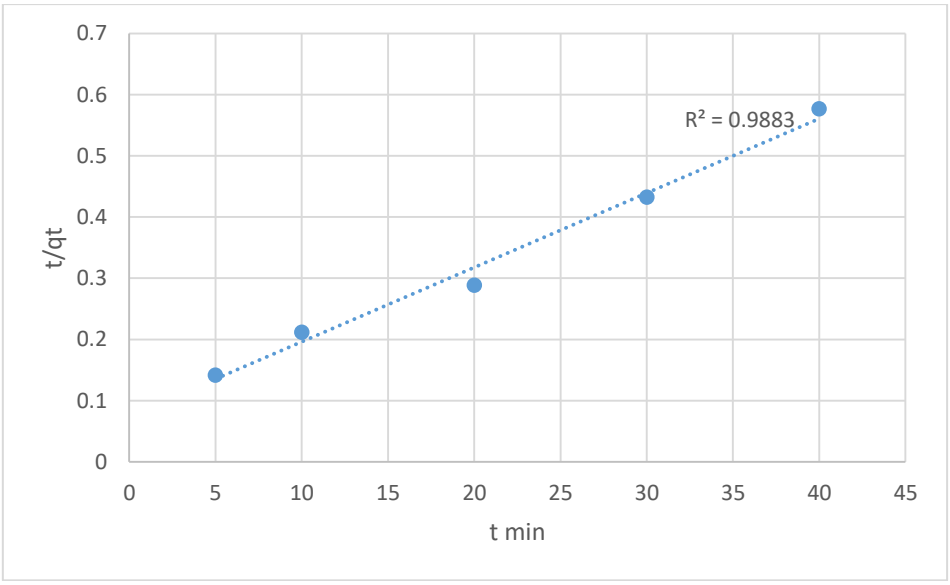


Figure **(4) Pseudo-second-order kinetics for Blue HB dye removal**
(Co: 50 mg/l, adsorbent dose: 5 mg up to 25 mg)

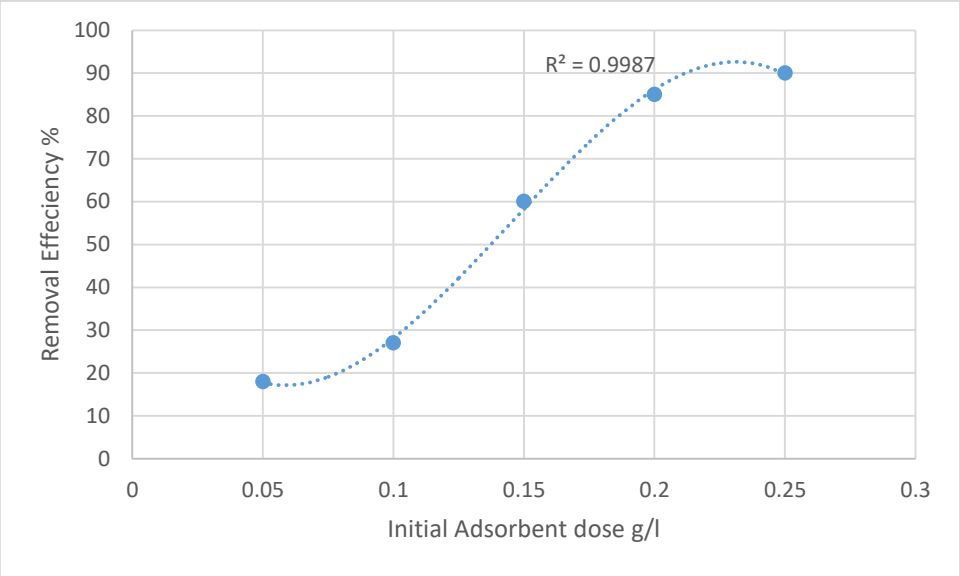


Figure **(5) Effect of initial adsorbent dose on removal efficiency**
(Co: 50 mg/l, adsorbent dose: 5 mg up to 25 mg, contact time: 40 min)

3.2.2 Effect of Contact Time

The impact of contact time on the HB blue dye removal was determined by using various dosages of hydroxyapatite, the result of removal efficiency displays in Figure (6). The optimum contact time for removal efficiency of 95 % is at 40 min. Nevertheless, additional contact time does not much affect the removal efficiency.

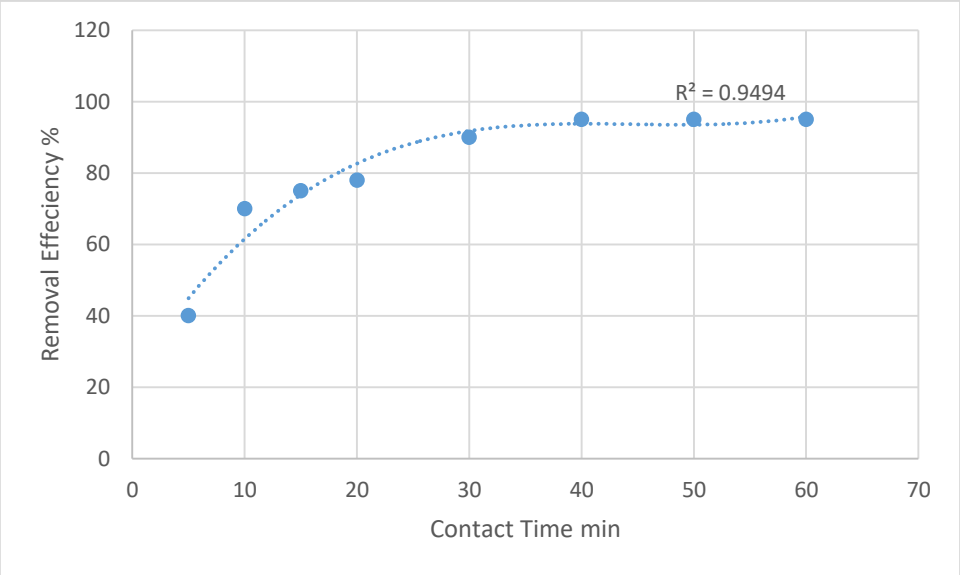


Figure **(6) Effect of contact time on removal efficiency**
(Co: 50 mg/l, adsorbent dose: 5 mg up to 25 mg, contact time: 40 min)

4. Conclusion

Textile industry produces voluminous quantities of dye containing wastewater which demand to be treated before being released to water ways. Thus, the use of bio waste (fish waste), as alternative for dye adsorption materials, can help both industries to handle the generated wastes in a way to eliminate any environmental impact. In the present study, hydroxyapatite from fish scales was used as an adsorption material for HB blue dye. The prepared hydroxyapatite was characterized using SEM, EDX

and FTIR. The “adsorption kinetics” was investigated using both “pseudo-first-order” model and “pseudo-second-order” model, and the time chosen to carry out the experiments for adsorption kinetics is 40 min. It was found that the “Langmuir model” showed the best correlation coefficients for the HB blue dye with R2 equals 1. It has been observed that HB dye option increased with the increase of the initial dosage, owing to the corresponding increase of the active sites available. The results showed that 20 mg where the removal efficiency achieved 85%.

Conflict of Interest

The authors declare that they have no conflict of interest.

Funding

I have no funding from any place.

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