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Adsorption efficiency of hydroxyapatite synthesised from black tilapia fish scales for chromium (VI) removal

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ABSTRACT

Water pollution is a major problem that impacts financial growth and socio-ecological sustainability of a country as well as health of the population. The presence of toxic heavy metals in wastewater such as chromium (Cr) (VI), copper, arsenic, lead, mercury, cadmium, etc. may lead to serious health issues. Therefore, this paper aims to synthesise natural hydroxyapatite (HAp) from black tilapia fish scales and investigate its efficiency as adsorbent for Cr (VI) removal. In this study, the black tilapia fish scales were soaked and washed thoroughly with distilled water to eliminate impurities such as dust and other particles, then dried in the oven before being alkaline treated for 1 h with a 50% NaOH at 100 °C. High purity HAp with an irregular rod-shape was successfully synthesised. The effectiveness of HAp from tilapia fish to remove Cr (VI) was tested at various initial concentrations (30–70 mg/L) and HAp dosages ranging from 2 to 6 g. The results discovered that the synthesised adsorbent had a substantial impact on the removal effectiveness of the Cr (VI) for both manipulated parameters; initial concentration and Cr (VI) pH. The optimum result for Cr (VI) removal rate was achieved at 61.43% at 60 min by using 6 g of HAp. Freundlich isotherm model shows greater suitability with higher R^2 = 0.995. Meanwhile, pseudo-second-order model is favourable for the adsorption process occurred in this study owing to its higher correlation coefficients. According to the findings of this study, black tilapia scale waste can be transformed into an effective adsorbent for Cr (VI) removal in wastewater treatment. This includes industries that may be exposed to Cr (VI), such as welding, coatings, plating, and textile production that use chromium-containing metals.

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1. Introduction

Water pollution is a problem that has an influence on a country's financial growth, socio-ecological sustainability, and population health. Although focus has been on water quantity, water-use effectiveness, and water distribution, nonetheless, poor administration of wastewater and agricultural drainage are among issues that cause poor quality of water and further leads to water crisis across the globe. The problem of water shortage is not only caused by the scarcity of asset, but also due to worsening of water quality in the basins that consequently decreases the safe water for consumption [1]. The impact of toxic by Cr (VI) is due to strong oxidizing effects that formed by several anions, which are dissolvable and mobile in nature. However, they are weakened to the soil under alkaline to slightly acidic conditions, resulting in high reactivity in the ground. In this way, 0.1 mg/L is the optimum concentration of Cr (VI) permitted in drinking water because of the toxicity nature of this compound and the potential oxidation of Cr (III) to Cr (VI) [2].

Heavy metals include cadmium (Cd), mercury (Hg), zinc (Zn), lead (Pb), and Cr, which are metals and metalloids with densities more than 5 g/cm^3. This sort of contamination not only debases the quality of surrounding environment, food crops, and water bodies, it also affecting the health and well-being of all living organism through the food chain [4]. The Cr exists in nature either as hexavalent Cr (VI) or trivalent Cr (III). In comparison to Cr (III), Cr (VI) is hazardous, genotoxic, mutagenic, carcinogenic, and

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causes skin lesions, ulceration, a nasal septum aperture, a perforated eardrum, decreased spermatogenesis, and lung cancer [3]. One of the biggest issues related to heavy metal contamination is the bioaccumulation and bio magnification exposure for living organisms in the surroundings environment. Therefore, most of the substances are regularly observed to provide fundamental data to accurately predict ecological health dangers.

Fresh water is a major environmental asset to the present world as water is the fundamental component in natural elements of human, animal, and plants [5]. Yearly, worldwide requirement for water has been expanding at a rate of about 1% as a component of populace development, financial advancement and changing consumption pattern among other factors. Domestic and industrial requirement for water grow more rapidly as compared to agricultural requirement, despite the agricultural industry being the largest consumer. The significant growth in the quantity of fish waste produced throughout the world has raised environmental concerns, with it estimated that almost two-thirds of the entire number of fish is wasted as trash [6–7]. Tilapia fish scales particularly contains vital compound known as hydroxyapatite (HAp) that can be used as an adsorbent. When exposed to high temperatures, hydroxyapatite (HAp) with chemical formula $Ca_{10}(PO_4)_6(OH)_2$ is a stable phase compared to other types of calcium phosphate. Among other various methods of extraction or synthesis of HAp are sol–gel, wet precipitation, mechanochemical, combustion, hydrothermal and natural resources. HAp is a highly promising compound used in various applications such as bone filler, soil treatment, biofuel, and as an effective biosorbent to remove toxic heavy metals in wastewater.

In this paper, the adsorption efficiency of HAp adsorbent synthesised from black tilapia fish scales for Cr (VI) removal was studied. The potential of HAp synthesised from black tilapia fish scales waste on the Cr (VI) removal rate under various HAp adsorbent dosages and Cr (VI) initial concentrations piqued researchers' attention.

2. Experimental procedures

2.1. Sample preparation

The material used in this study was black tilapia fish scales purchased from Lazada, Malaysia. Firstly, the black tilapia fish scales were pre-treated by soaking and washing using distilled water to remove the impurities such as dust and any other particles followed by drying by exposing it to direct sunlight for 3 days. Then, the dried black tilapia scales were deproteinized through pretreatment for 12 h in 0.1 M HCl (Hmbg, 37%) [8].

2.2. Alkaline treatment

The tilapia scales were treated using NaOH solution (QRëc). In this treatment, 1:14 (w/v) of fish scales were stirred in 5% NaOH solution at 400 rpm at 70 °C for 5 h [9]. After that, the white precipitates were filtered and cleaned by using distilled water before drying for 1 h at 100 °C. Subsequently, the white precipitates were treated for 1 h with a 50% NaOH in a 1:6 (w/v) ratio at 100 °C. To ensure the produced solution is clear, filtration process was repeated several times following by rinsed the solution with distilled water. Later, the filtered white precipitates were dissolved using 200 mL distilled water and the pH was altered to pH 7 using H_3PO_4 (85%, Bendosen) with 0.1 M molarity. Finally, the solution was agitated constantly for 1 h and then dried for 2 h at 100 °C in order to produce the HAp adsorbent.

2.3. Adsorption test

Cr (VI) removal experiments were done in a beaker using hot plate magnetic stirrer at 170 rpm. Adsorption tests were done at pH 5 with changed initial concentrations (30–70 mg/L) and HAp dosage of 2–6 g. In 500 mL of distilled water, potassium dichromate ($K_2Cr_2O_7$) was used to make a Cr (VI) stock solution. To begin, in a 1000 mL volumetric flask, a 300 mg/L stock solution of Cr (IV) was prepared by liquifying the $K_2Cr_2O_7$ (ChemAR). Then again, by using a 1000 mL volumetric flask, the $K_2Cr_2O_7$ solution was weakened to the required concentration. Subsequently, the sample was mixed using hot plate magnetic stirrer at 170 rpm. The sample was collected and filtered at predetermined time intervals before the Cr (IV) content being analysed using UV–Visible spectroscopy at 540 nm [10]. Eqs. (1) and (2) were used to compute the quantity of Cr (IV) adsorb per gram as well as the Cr (IV) removal percentage by the adsorbent [11].

$$q_e = \frac{V\ (C_o\text{-}C_e)}{W} \tag{1}$$

$$\text{Adsorption}\ (\%) = \frac{(C_o\text{- }C_e)}{C_o} x100 \tag{2}$$

where q_e (mg/g) denotes the quantity of metal ions, V denotes the solution volume (L), W the adsorbent dosage (g), C_o (mg/l) denotes the initial Cr (IV) concentration, and C_e (mg/L) denotes the equilibrium Cr (IV) concentration in solution.

2.4. Characterisation

Mineralogy of the HAp adsorbent was examined using X-ray diffraction (D8 Advance, Bruker) with Cu-Kα (λ = 1.5406 A) at 40 kV accelerating voltage and 40 mA of current in the range 2θ between 20° to 80°. The phase identification was done by comparing the obtained XRD pattern with HAp pattern (ICDD 00–003-0747). FESEM (JFM-7600F, JEOL, Japan) running at 15 kV accelerating voltage was used to analyse the microstructure and its size. The elemental deposition of the HAp adsorbent was determined using the EDS with a 20 mm working distance at 20 kV accelerating voltage. In the meanwhile, the Cr (VI) concentration was defined using inductively coupled plasma/optical emission spectrometry (ICP/OES).

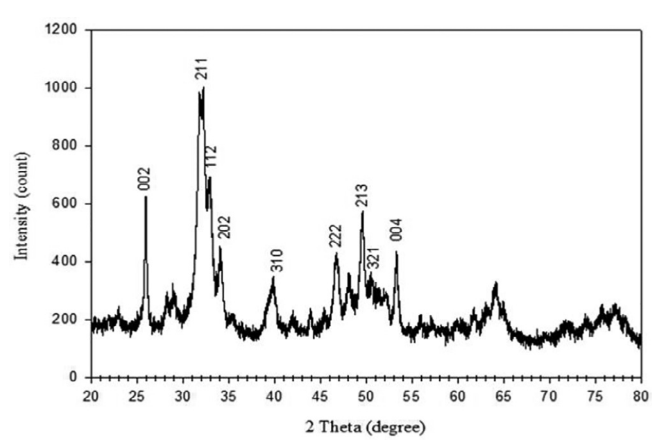

Fig. 1. XRD pattern of the HAp synthesized from black tilapia fish scales via alkaline treatment.

3. Results and discussion

3.1. Synthesised HAp adsorbent characterisation

Fig. 1 shows the XRD pattern of HAp synthesised from black tilapia fish scales via alkaline treatment. The HAp standard (ICDD 00-003-0747) was used to accomplish spectral verification. As shown in Fig. 1, all peaks of HAp synthesised from black tilapia fish scale match to the HAp standard peak. All chemical components and collagen in the fish scale were removed by alkaline heat treatment, resulting in pure HAp adsorbent. In addition, the HAp adsorbent obtained in this study exhibits low crystallinity, where low and broad peaks can be seen on XRD pattern as shown in Fig. 1. Low crystalline HAp was more metabolically active and had a faster biodegradation rate than high crystalline HAp [12].

The morphology of the synthesised HAp is depicted in Fig. 2, which has an irregular rod shape and a crystal size. The rod shape had a width ranging from 50 to 60 nm and length in between 30 and 200 nm. Kongsri et al. [9] found that HAp synthesised from fish scale waste has similar hexagonal crystal shape with average crystal size of 20 nm.

Fig. 3 shows the elemental analysis of the synthesised HAp adsorbent which contains elements such as Ca, P, and O which represent the calcium, phosphate, and oxygen respectively. According to the obtained spectra, the Ca/P ratio of the synthesised HAp adsorbent is 1.75, whereas the Ca/P ratio of the stoichiometric HAp is 1.67. The existence of β-type carbonate hydroxyapatite, which replaces phosphate ions with calcium ions, may explain the synthesised HAp adsorbent's high Ca/P ratio [13].

3.2. Cr (VI) adsorption efficiency

Cr (VI) removal using different adsorbent dosages (2, 4, 6 g) of HAp synthesised from black tilapia fish scales at pH 5 is presented in Fig. 4(a). The results can be observed into two stages. The first stage is rapid Cr (VI) removal that occurs at first 5 mins of contact time between HAp adsorbent and Cr (VI) solution. In Fig. 4(a), a rapid adsorption of Cr (VI) was observed on 6 g of HAp adsorbent 50.71% removal from the initial concentration of 70 ppm. Similar trend was observed for 2 g and 4 g dosage of HAp adsorbent. In addition, slow Cr (VI) removal stage occurs at contact time more than 5 min. At this stage, minimal removal of less than 15% Cr (VI) at slow pace of time was recorded within 55 min contact time. Although the adsorption rate is less efficient at this stage, it is still crucial in providing overall optimum removal rate value of Cr (VI) solution. Adsorbent with 6 g of dosage managed to adsorb more Cr (VI) till the end of set time compared to others. This is feasible because adsorbent dosage is a critical component in the adsorption process as the active surface area and number of adsorption sites grow [14]. This also determines the amount of removal and economics of the process. The higher the adsorbent dosage used; the more Cr (VI) ion adsorption sites are facilitated [15–16].

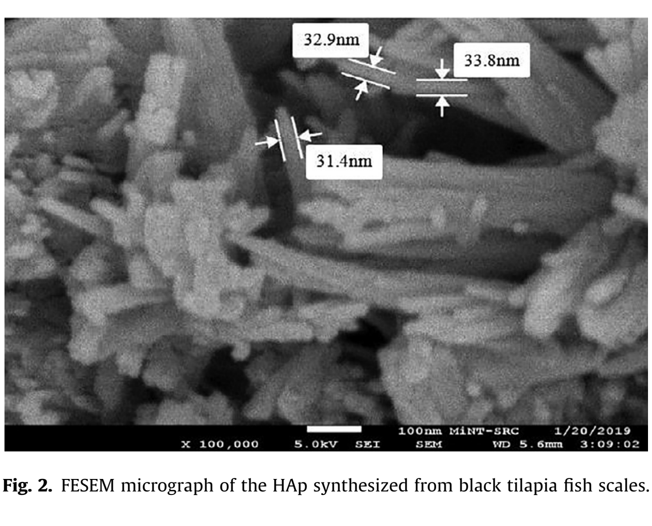

Fig. 2. FESEM micrograph of the HAp synthesized from black tilapia fish scales.

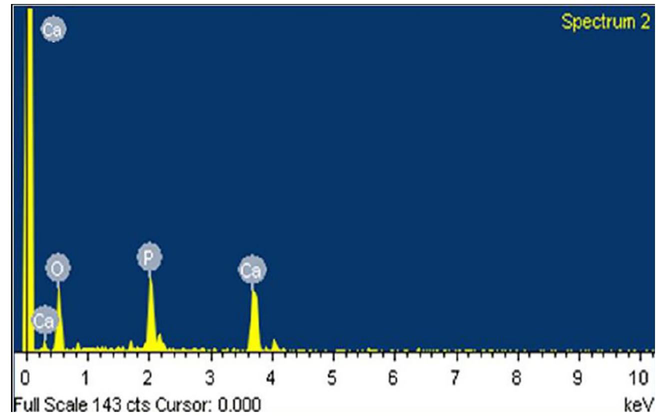

Fig. 3. EDS spectrum of the HAp synthesized from black tilapia fish scales.

Meanwhile, Fig. 4(b) shows the effect of 6 g HAp adsorbent on the removal efficiency of Cr (VI) at varied Cr (VI) initial concentrations. This graph also indicates similar phenomenon as in Fig. 4 (a), where there are two removal process stages of Cr (VI). For the effect of initial concentration of Cr (VI), the total removal for Cr (VI) initial concentration ranging from 30 to 70 ppm is almost similar whereby the difference is not more than 7%. This indicates that the initial concentration gives insignificant effect to the Cr (VI) removal process. Yet, Cr (VI) with initial concentration of 50 ppm shows optimum Cr (VI) removal of 70% after 60 min, followed by 30 ppm and 70 ppm, respectively. This proved that the total available adsorption sites would be relatively stable for a fixed adsorption dosage even the initial concentration of Cr (VI) being manipulated. Therefore, increasing the Cr (VI) concentration resulted in insignificant effect on the Cr (VI) removal efficiency.

3.3. Isotherm adsorption

The two most frequently used isotherm models to ascertain the sorption capacity of the adsorption process are Langmuir and Freundlich [17]. The Langmuir isotherm model is used to define monolayer adsorption occurred on the surface of adsorbent. Meanwhile, Freundlich isotherm model is valid for a multilayer adsorption on heterogeneous surfaces of adsorbent [18]. It was discovered that the adsorption capacity (q_{max}) for Cr (VI) is 1.38 mg/g, which was greater than the other low-cost adsorbents [19]. The Langmuir isotherm is favourable due to the R_L value that lies between 0 and 1 [10]. It is also found that the Freundlich affinity constant (K_f) is 1.86. The heterogeneity value (1/n) found in this study is 0.519, indicating that the adsorption conditions were favourable due to the usual distribution of active adsorption sites [20]. This value also shows the nature of the process, which is physisorption. Physisorption is primarily caused by the presence of a van der Waals bond between the adsorbent and the adsorbate [21]. The n rate greater than one indicates a strong energetic interaction and reactivity, which is advantageous for effective adsorption [22]. Fig. 5 shows the corresponding Langmuir and Freundlich isotherms graphs and Table 1 shows the parameters for both isotherm models. This study indicates greater suitability of the Freundlich isotherm owing to its higher correlation coefficients, R^2 = 0.995.

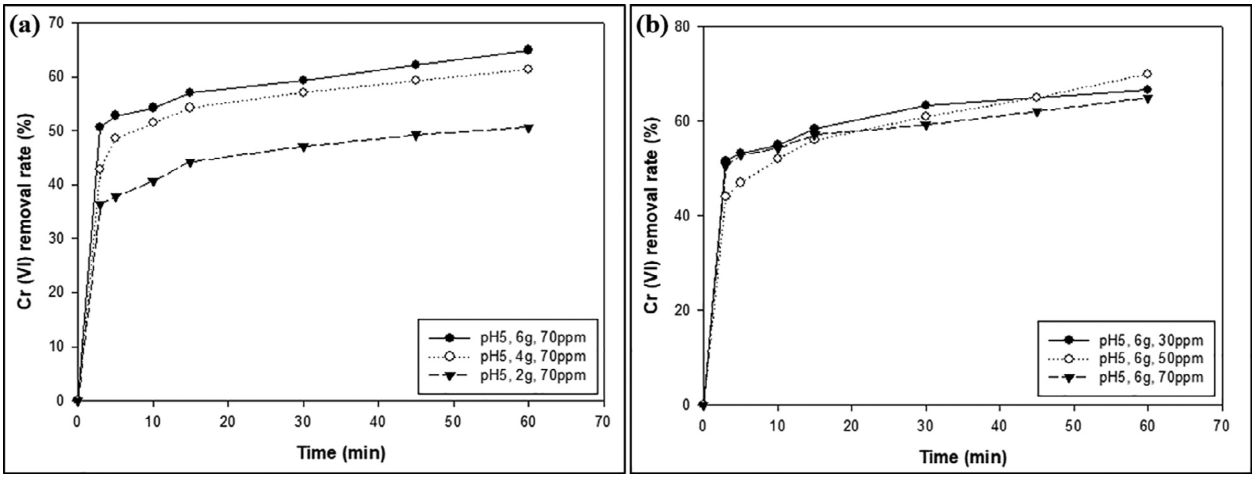

Fig. 4. The comparison of Cr (VI) removal rate efficiency by different: (a) HAp dosage, and (b) Cr (VI) initial concentration.

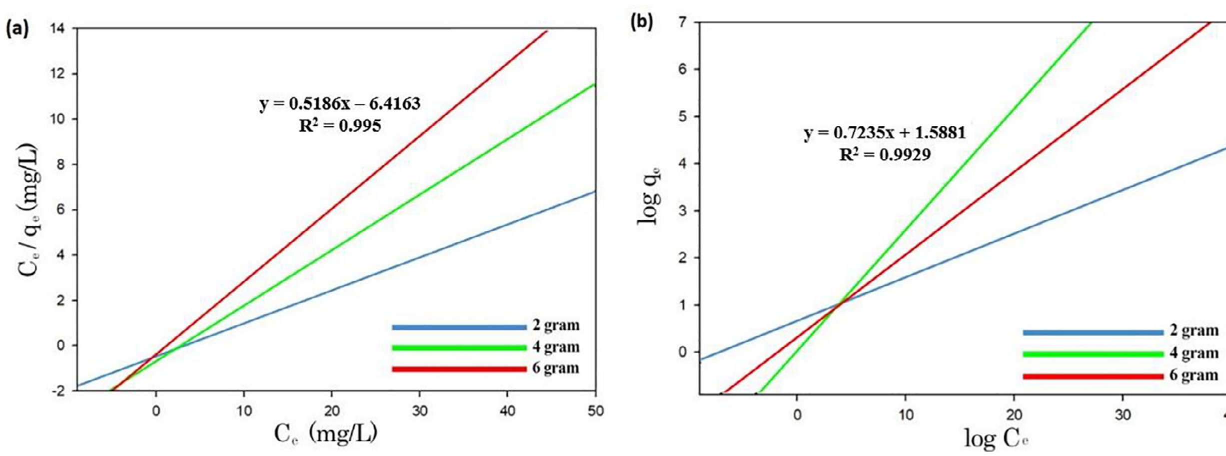

Fig. 5. Adsorption of Cr (VI) by (a) Langmuir and (b) Freundlich isotherm model.

Table 1
Langmuir and Freundlich constants and correlation coefficients for adsorption of Cr (VI).

Langmuir				Freundlich		
q_{max}	b	R^2	R_L	K_F	1/n	R^2
1.382	0.4644	0.9923	0.003	1.8588	0.5187	0.995

3.4. Kinetic adsorption

Pseudo-first-order and pseudo-second-order kinetic model are used to determine the mechanism of kinetic adsorption in this study. Pseudo-first-order model was employed in liquid/solid systems where the change in surface rate is proportional to the remaining surface sites number. Meanwhile, when the rate is proportional to the square of the surface locations, the pseudo-second-order model is true [23–24]. Fig. 6 and Table 2 show the linearized plots of the kinetic models are presented and the parameters for both models respectively. The pseudo-second-order model is advantageous and best represented the adsorption process due to its greater correlation coefficient [25]. The maximum Cr (VI) ion adsorbed (q_e) is 8.156 mg/g. According to the pseudo-second-order kinetic model, adsorption was a chemisorption process involving ion exchange and valency forces between the adsorbent and adsorbate [26]. This reaction is crucial in waste water treatment, particularly in heavy metal removal, since it provides more active and accessible sites for adsorption to occur efficiently.

4. Conclusions

The current work shows that HAp adsorbent can be effectively produced from black tilapia fish scales utilising alkaline treatment. Pure HAp adsorbent with irregular rod-shaped crystals varying in size from 50 to 60 nm width to 30–200 nm length was synthesised. Besides that, the synthesised HAp adsorbent has low crystallinity. Higher dosage of HAp adsorbents enhanced the number of active sites for removal of Cr (VI). The optimum result for Cr (VI) removal rate was achieved at 61.43% within 60 min by using a 6 g of HAp adsorbent. In addition, there is no significant outcome of different Cr (VI) initial concentration as the results did not vary more than 7% compared to others. According to kinetic adsorption analyses, the pseudo-second order model best fits the adsorption that happened and Freundlich isotherm model is favourable with higher

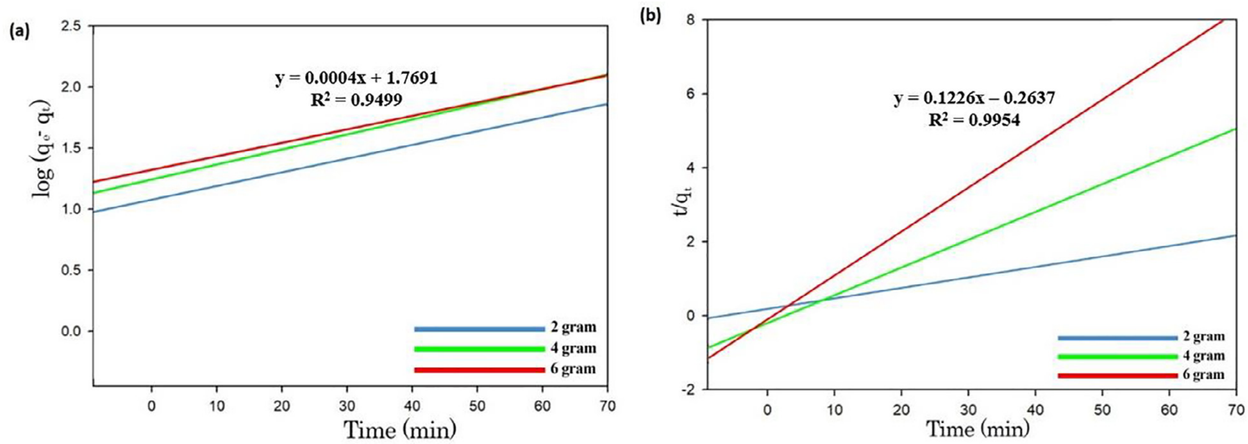

Fig. 6. Linearized plot of experimental data using (a) pseudo-first order model and (b) pseudo-second order model.

Table 2
Parameters of pseudo-first order and pseudo-second order models.

Psuedo-First Order			Psuedo-Second Order		
q_e	K_1	R^2	q_e	K_2	R^2
7.8240	0.0009	0.9499	8.1566	0.057	0.995

correlation coefficient of 0.99. Therefore, the outcomes of this study show that HAp adsorbent produced from the scales of black tilapia has significant potential to be turned into a wastewater treatment adsorbent. In addition, conversion of waste materials into a valuable material is expected to provide effective waste management approach to the black tilapia fish production industry. Welding, textile, pigments, spray paints, coatings, and other hot operations on chromium-containing metals are among the industries that may profit.

CRediT authorship contribution statement

M.A. Selimin: Writing – original draft, Formal analysis. **A.F.A. Latif:** Writing – original draft, Visualization, Investigation. **C.W. Lee:** Investigation. **M.S. Muhamad:** Writing – review & editing, Funding acquisition, Validation. **H. Basri:** Writing – review & editing, Validation. **T.C. Lee:** Conceptualization, Methodology, Supervision, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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