INTRODUCTION

At present, the environmental problems are tremendously increasing in Thailand due to technological advancements. This has led to the expelling of many toxins and wastes from the automobile industries, chemical fertilizers and pesticides contaminated with heavy metals from agricultural domains, laboratory chemicals and hazardous wastewater from scientific labs [1]. The wastewater contaminated with such inorganic and organic substances, as well as heavy metals, are not treated before discharging into natural water sources. This unhealthy practice causes serious impacts on the environment and human health [2].

Chromium contaminants, either in Cr(III) or Cr(VI) form, in water sources cause high toxicity [3]. It is more than a hundred times more toxic than Cr(III). Once, Cr(VI) enters the human body, it will accumulate, causing chronic toxicity and cancer in various organs. On the other hand, Cr(III) helps the metabolism of fats and sugars in the human body, but if taken in large quantities, it causes harm. If animals are fed with chromium contaminated food, especially Cr(VI), even in small doses, it retards their growth and may even lead to cancer [4-6]. Therefore, it is necessary to remove chromium ions from wastewater before releasing it into natural water sources. There are several treatment processes, such as chemical reduction [7], membrane separation [8], ion-exchange [9] and adsorption [10]. Among all the separation processes, adsorption is the most suitable one for chromium ions removal. However, the challenge is to fabricate an efficient and environmentally friendly adsorbent. The most used adsorbents for heavy metal removal are clay, silica, zeolite, activated carbon and cellulose [11,12]. It is possible to derive better adsorption performances from these adsorbent materials by improving their surfaces. The detection of bioactive substances, for ZnO nanoparticles, with high surface area and having good catalytic, non-toxic and antibacterial properties is an emerging field of study. This prompted us to study the adsorbent efficiency of waste material of cellulose obtained from bamboo chopsticks was combined with ZnO (Cel-ZnO) to prepare an optimized adsorbent.
chopsticks from the local market of Buriram, Thailand. All chemicals were of analytical grade and used without purification.

A thermo scientific spectrometer (Thermo Nexus 470FT-IR, Nicorette, USA) was used to obtain the Fourier transform infrared (FT-IR) spectra of different materials in the range 4000-400 cm⁻¹, while a scanning electron microscope equipped (Hitachi FE-SEMS-4800) was used to determine their surface morphologies. Thermogravimetric analyses (TGA) were performed using a Thermo Scientific SDT Q600 series thermogravimetric analyzer (TA instrument).

Synthesis of Cel-ZnO adsorbent: Bamboo chopsticks were cut into smaller particles and spun to get fibres with even smaller particle sizes. Hemicellulose and lignin were then removed by base pre-treatment to make cellulose fibres purer. Initially, 5 g of cellulose fibre was immersed in Zn(CH₃COO)₂ ·2H₂O for 1 h under continuous stirring at 200 rpm. The mixture was then sonicated for 20 min in a water bath and followed by NaOH pre-treatment for 10 min to reduce zinc nanoparticles. It was then annealed for 24 h at 30 ºC. Finally, at this stage, cellulose zinc oxide was obtained as the product and had been used thereafter for further Cr(VI) absorption studies [13].

Optimized conditions

Effect of pH: Approximately 0.005 g of the adsorbed sample was weighed and immersed in a 50 mL Cr(VI) solution of concentration 250 mg/L with varying pH levels from 2 to 7. It was then shaken at a speed of 150 rpm for 360 min. The mixtures were centrifuged and the resulting solutions were further analyzed.

Effect of time: Approximately 0.005 g of the adsorbed sample was weighed and immersed in a 50 mL Cr(VI) solution of concentration 250 mg/L at a pH level of 3 and shaken at a speed of 150 rpm for different time durations. The time durations employed for the study were 1, 3, 5, 10, 20, 30, 60, 180 and 360 min. The resultant mixture solutions were centrifuged and subjected to further analysis.

Effect of concentration: Approximately 0.005 g of adsorbed sample was weighed and immersed in 50 mL Cr(VI) solution of varying concentrations (10, 25, 50, 100, 150, 200, 250, 300 and 500 mg/L) at pH 3 and shaken at a speed of 150 rpm for 360 min. The resultant solutions from each mixture were centrifuged and examined for further analysis.

Adsorption studies: To measure the concentration of Cr(VI) solution adsorbed, the sample solution was immersed in comparison to the standard solution of potassium dichromate. A 1:5 ratio of Cr(V) to 1,5-diphenylcarbazide (DPC) solution was used to form a purple complex. The absorbance was measured using a UV-Vis spectrophotometer. At a wavelength of 540 nm, the amount of Cr(VI) absorbed (q) was calculated as follows [14-16]:

\[
Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)
\]

\[
C_e = \frac{1}{bQ_m + \frac{C_s}{Q_m}} \quad (2)
\]

\[
\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)
\]

where \( Q_e \) (mg/g) represents adsorption capacity, \( C_0 \) and \( C_e \) represent the initial and equilibrium concentrations of Cr(VI) (mg/L), respectively, \( V \) represents the volume of the solution; \( m \) represents the weight of adsorbent; \( Q_m \) is the Langmuir monolayer sorption capacity; \( b \) (L/mg) is the Langmuir equilibrium adsorption constant; \( K_f \) and \( n \) are the Freundlich equilibrium adsorption constants; \( Q_e \) is the amount of adsorbed in mg/g at time \( t \) (min); \( k_1 \) (min⁻¹) is the rate constant of pseudo-first-order adsorption and \( k_2 \) (g/mg-min) is the pseudo-second-order rate constant.

Recyclability studies: In this experiment, desorption of Cr(VI) from the prepared adsorbent (Cel-ZnO) was performed using deionized water as solvent washing regeneration incorporated with thermal treatment method. The spent adsorbents were dipped at 80 °C for 30 min then followed by drying at 105 °C for 10 h in an oven. The optimal conditions were maintained throughout the reusability experiments.

RESULTS AND DISCUSSION

FTIR studies: The FTIR analysis of Cel and Cel-ZnO was performed and compared (Fig. 1). The cellulose showed a broad peak appeared at 3437 cm⁻¹, which was characteristic stretched oscillations of cellulose O-H bonds. Moreover, the peaks at 1730 and 1434 cm⁻¹ were due to the stretched oscillations of the C=O after the elimination of hemicellulose upon base extraction. In Cel-ZnO adsorbent, a sharp and intense band at 540 cm⁻¹ indicates the existence of the Zn-O vibrations [18].

Morphology: The surface area characterization of Cel, Cel-Cr, Cel-ZnO and Cel-ZnO-Cr using SEM technique is shown in Fig. 2a-d. It was found that base treatment makes the cellulose surface more suitable for adsorption and the ZnO solution makes the surface more favourable to adsorb chromium metal.

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\[
\ln\left(\frac{Q_e}{Q_{e,0}}\right) = \ln Q_e - (k_1)t \quad (4)
\]

\[
t = \frac{1}{Q_{e,0}^2} + \frac{t}{Q_{e,0}} \quad (5)
\]
Thermal studies: TGA was used to determine the weight loss and weight change with temperature of Cel and Cel-ZnO. It was found that Cel and Cel-ZnO began to lose its weight at 260 ºC upon heating. For Cel and Cel-ZnO, the maximum weight loss occurred at 320.70 and 289.55 ºC, respectively. The ash residue of Cel-ZnO after combustion was about 21.39%, which was 16.07% more than cellulose (Fig. 3). It has been found that as a result of zinc oxide embedded in cellulose, the ash content of burned wood containing Cel-ZnO is higher than that of cellulose (Table-1) [19].

Optimization of adsorption conditions

Effect of pH: The adsorption capacity of Cel and Cel-ZnO towards Cr(VI) metal ion in the K₂Cr₂O₇ solution was studied at different pH values. At pH 3, both Cel and Cel-ZnO reached their maximal adsorption capacities of 122.26 and 253.66 mg/g when exposed to Cr(VI) solution. Since the surface of the adsorbent is protonated in a very acidic solution, the adsorption capabilities decreased with increasing solution pH (Fig. 4). However, when the surface pH is low, the adsorption capacity is also reduced due to competition between Cr(VI) ions and H⁺ ions. Adsorption decreases above a pH of 3, because chromium is poorly soluble in alkaline solutions and hence precipitates out [20].
Effect of initial concentration: Different concentrations of dichromate solution were used to examine the adsorption capacities of Cel and Cel-ZnO sorbents towards Cr(VI) metal ion. Adsorption of 0.005 g of sorbent took 360 min at initial solution concentrations of 10, 25, 50, 100, 150, 200, 250, 300, and 500 mg/L. As can be seen from Fig. 5, both Cel and Cel-ZnO showed increasing adsorption capacities when Cr(VI) ion concentrations increases, while the latter maintained a steady adsorption capacity at 250 mg/L. Under these circumstances, the Cr(VI) adsorption capabilities of Cel and Cel-ZnO were 121.64 and 253.59 mg/g. Since, the surface area of Cel and Cel-ZnO does not change with the concentration of chromium ions in the solution, further adsorption is restricted [21].

Effect of time and temperature: Studies were conducted on the adsorption capacity of Cel and Cel-ZnO sorbents for Cr(VI) in a dichromate solution for 1, 3, 5, 10, 20, 30, 60, 180, and 360 min (Fig. 6). The solution concentration was set at 250 mg/L, and the adsorption temperatures were maintained at 30, 40 and 50 ºC. For all of the considered reaction conditions, the adsorption efficiency of Cel did not change with the temperature. As temperatures increased, however, Cel-ZnO lost some of its adsorption efficiency. Adsorption efficiency towards Cr(VI) was shown to rapidly increase within the first 30 min, before stabilizing at a high level. There were consistent patterns across all the studied three temperature ranges. Due to the high surface area of the adsorbent, the adsorption volume continues to increase until it reaches a steady state after the adsorption area volume is exhausted [22].

Kinetics studies: Fig. 7 displays the adsorption kinetics using pseudo-first-order and pseudo-second-order equations. By modifying the time required to attain the adsorption equilibrium while altering the reactant concentration, the adsorption mechanism could be identified. Thus, the reaction order and the correlation coefficient were calculated (Table-2). Consistent with the pseudo-second-order equation, it has been found that Cel and Cel-ZnO establish new chemical interaction during adsorption [23]. It results from the heavy metal ion and the adsorbent exchanging or giving each other electrons. Adsorption process based on Cel and Cel-ZnO sorbents responds at a rate proportional to the square of the reactant concentration.

Absorption isotherm studies: The adsorption isotherm was determined to correlate the amount of Cr(VI) adsorbed per weight of Cel-ZnO with the Cr(VI) concentration. When
comparing the Langmuir and Freundlich isotherm graphs (Fig. 8a-d), it was found that the correlation coefficient is very near to one (Table-3). As predicted by the Langmuir model, in case of cellulose, the adsorption process is homogenous and mono-layer in nature, with a correlation coefficient of 0.9849. The adsorption mechanism of Cr(VI) on Cel-ZnO, however, was shown to be compatible with the Freundlich model and exhibited the heterogeneous and multi-layered adsorption [24].
Reuseability studies: The efficiency of Cel and Cel-ZnO adsorbents was studied. The dichromate solution was readsorbed with an adsorption time of 360 min, 250 mg/L initial concentration of the solution and an adsorbent amount of 0.005 g at 30 °C (Fig. 9). The Cel and Cel-ZnO adsorbents exhibited maximum efficiency for the first adsorption cycle and adsorbed less for further cycles. The adsorbents were reused for five consecutive cycles for the removal of Cr(VI) ions, showing that Cel-ZnO has good adsorption efficiency when reused [25].

Comparison studies: Table-4 provides a comparison of the maximum monolayer adsorption capacity (q_{max}) of different adsorbents towards Cr(VI) ions with the current adsorbents. The results showed that the maximum adsorption capacity of Cel-ZnO in the present work is more than all the other ZnO obtained from different sources [26-31]. It is revealed that Cel-ZnO could be considered as a better candidate for removing Cr(VI) ions from wastewaters.

<table>
<thead>
<tr>
<th>Adsorbent types</th>
<th>q_{max} (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose-TiO_{2}/REC</td>
<td>69.81</td>
<td>[26]</td>
</tr>
<tr>
<td>Biochar/nano-iron oxide composite</td>
<td>55.00</td>
<td>[27]</td>
</tr>
<tr>
<td>FeS/chitosan/biochar composite</td>
<td>103.93</td>
<td>[28]</td>
</tr>
<tr>
<td>Amino-functionalized magnetic cellulose</td>
<td>171.50</td>
<td>[29]</td>
</tr>
<tr>
<td>Magnetic pine cone composite</td>
<td>15.24</td>
<td>[30]</td>
</tr>
<tr>
<td>Polyvinylimidazole modified cellulose</td>
<td>134.00</td>
<td>[31]</td>
</tr>
<tr>
<td>Cel-ZnO</td>
<td>197.26</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Conclusion

The adsorption efficiency of the new Cel-ZnO adsorbent prepared from the used bamboo chopsticks were confirmed for the functional groups and morphological characteristics. Moreover, the optimum adsorption conditions were determined by studying the effect of various factors. By modifying the surface morphology of Cel-ZnO sorbent, base treatment renders the cellulose surface more amenable to adsorption. As a result, the surface has a tendency to uptake in Cr(VI) more effectively. It was determined that an adsorbent quantity of 0.005 g, an initial concentration of chromium of 250 mg/L, a pH of 3 and an adsorption duration of 360 min at 30 ºC were optimal conditions for Cr(VI) metal ion adsorption. Compared to Cel-ZnO, which was determined that an adsorbent quantity of 0.005 g, an initial concentration of chromium of 250 mg/L, a pH of 3 and an adsorption duration of 360 min at 30 ºC were optimal conditions for Cr(VI) metal ion adsorption. Compared to Cel-ZnO, which adsorption duration of 360 min at 30 ºC were optimal conditions for Cr(VI) metal ion adsorption. Compared to Cel-ZnO, which adsorption duration of 360 min at 30 ºC were optimal conditions for Cr(VI) metal ion adsorption. Compared to Cel-ZnO, which adsorption duration of 360 min at 30 ºC were optimal conditions for Cr(VI) metal ion adsorption. Compared to Cel-ZnO, which adsorption duration of 360 min at 30 ºC were optimal conditions for Cr(VI) metal ion adsorption. Compared to Cel-ZnO, which adsorption duration of 360 min at 30 ºC were optimal conditions for Cr(VI) metal ion adsorption. Compared to Cel-ZnO, which adsorption duration of 360 min at 30 ºC were optimal conditions for Cr(VI) metal ion adsorption.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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