Removal of Cr (III) from industrial wastewater using coconut shell carbon and limestone as adsorbent

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Abstract. Agricultural waste materials gained attention among researchers to study the effectiveness of adsorbent media in heavy metal treatment. In this study, application of coconut shell carbon and limestone as modified adsorbent was used to remove Cr (III) from industrial wastewater. Synthetic industrial wastewater sample containing 2 mg/L of Cr (III) was prepared using distilled water and standard solution of Cr (III). Batch adsorption study was conducted to determine the effect of varied contact time (0 to 120 minutes) and pH (pH3 to pH7). The result shows that at 60 minutes of contact hour, the removal of Cr (III) from the synthetic industrial wastewater is about 98% with optimum adsorption capacity is 0.000019 mg/g at 250 rpm of agitation speed in pH5 as optimum pH. The kinetic data obtained specified that the data follow closely the pseudo-second-order. Thus, this indicates that mixing coconut shell carbon and limestone as a modified adsorbent has a potential in reducing Cr (III) concentration in industrial wastewater.

1. Introduction

Enormous industrialization with population growth and unplanned urbanization has contributed to severe water pollution. Excessive presence of heavy metals such as zinc, copper, nickel, mercury, cadmium, lead and chromium in the water will interfere quality of water and endanger the human health. High toxicity of heavy metals waste is generated from industries such as steel, electroplating, batteries manufacturing, dye production and paint. High concentration of Cr (III) may affect health problems such as ulcer, skin irritation, liver and kidney damage, nausea, vomiting, severe diarrhoea, respiratory tract and lungs carcinoma [1-3]. According to World Health Organization, the effluent from industries must comply with raw and drinking water standard which concentration of Cr (III) must not exceed maximum permissible limit of 0.05 mg/L. Thus, heavy metal treatment is necessary to overcome hazardous of pollutant in industrial wastewater.

There are several treatment technologies existing in treating heavy metals polluted in industrial wastewater such as physical, chemical and biological processes. In heavy metal treatment, the pollutant may be separated from the wastewater by using precipitation with hydroxide, ion exchange, reverse osmosis, electro dialysis, oxidation and reduction and adsorption [4]. Physical methods such as adsorption process is the most popular and economical alternatives for treating heavy metal pollutants from industrial wastewater [5]. Currently, application of activated carbon is widely used as adsorbent media for heavy metal treatment. Agricultural waste material from pistachio shell [6], banana peel [7], sweet potato peel [8], nut shell, rubber seeds, rice husks [9,10] and coconut shell processed into active carbons as agricultural by-product can be one of the chosen methods in treating heavy metal pollutants.
[11]. Most of agricultural waste materials containing cellulose has superior sorption capacity for various contaminants and being economic and eco-friendly product due to their unique chemical composition, obtainable in abundance, renewable nature and low-cost adsorbent for water and wastewater remediation [12].

Moreover, adsorbent from natural minerals such as siderite [13], hematite, laterite [14], goethite and limestone [15] also acts as an effective adsorbent in heavy metal removal. Most of researchers found that limestone was very effective adsorbent and has a potential to remove more than 90% of heavy metal such as Cd, Cu, Cr, Pb, Zn, Mn and Ni in water and wastewater [15-18]. Furthermore, from previous study, it is found that activated carbon prepared from coconut shell also has a potential in removing Pb [19]. However, no study has been done on the mixture of coconut shell carbon and limestone media for Cr (III) removal in industrial wastewater. Thus, in this study the potential of modified coconut shell carbon was explored by mixing the coconut shell carbon and limestone media. Batch adsorption experiment was conducted to determine the effect of varied pH and contact time of modified adsorbent media. The aim of this paper is to determine the effectiveness of mixing limestone and coconut shell carbon as modified natural adsorbent for Cr (III) removal.

2. Methodology

2.1. Adsorbent preparation

Coconut shell carbon was manually prepared in the laboratory from coconut shell. The shell was burned in the muffle furnace at a temperature of 350⁰C for 10 minutes. The carbon was left in the oven at a temperature of 110⁰C for 24 hours to reduce the temperature. The coconut shell carbon was ground by using a heavy-duty blender. Both of limestone and coconut shell carbons were sieved to obtain particle size in the range of 2 to 5mm.

2.2. Batch study adsorption

Batch study adsorption was carried out to determine the removal efficiency and capacity of modified adsorbent media to adsorb Cr (III) in wastewater. A standard solution of chromium was prepared using stock solution 1000 mg/L (ppm). The synthetic sample was prepared by dissolving Cr (III) solutions into deionized water to obtain initial concentration of 2mg/L of Cr (III). 100 ml diluted solution is prepared in a 250 ml of volumetric flask. Thus, dilution equation to determine the concentration of heavy metals in synthetic waste water is shows in equation (1).

\[
\text{The concentration of heavy metals} = \frac{\text{required ppm (mg/L)} \times \text{required volume (mL)}}{\text{stock of solution 1000 ppm (mg/L)}}
\]  

(1)

The effect of contact time ranging from 0 to 120 minutes and pH ranging from pH3 to pH7 were investigated in this study. In this study, fixed sample was prepared by mixing 32g of coconut shell carbon and 71g of limestone media using orbital shaker. After agitation process, 20 mL of sample was drawn from supernatant and acidified using 1% of concentrated nitric acid, HNO₃. The concentration of both heavy metals was measured using Atomic Absorption Spectrophotometer (Brand: Shimatzu, Model: AA-6800). The removal efficiency of the adsorbent media was presented in the equation (2).

\[
\% \text{ removal} = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]  

(2)
The adsorption capacity of adsorbent media can be expressed in equation (3).

\[ q_e = \frac{(C_i - C_t)V}{m} \]  

(3)

Where \( C_i \) and \( C_t \) are the initial and final concentration of heavy metal pollutant sample (mg/L), \( V \) is the volume of sample (L) and \( m \) is the mass of adsorbent (g).

2.3. Kinetic study

From the adsorption equilibrium study, the behaviour of adsorption mechanism then is analysed using pseudo-first order and pseudo-second order kinetic model. Kinetic study is a mathematical model to describe the adsorption behaviour and the mechanism of adsorbent onto adsorbate. The determination of the kinetic parameters of adsorption of Cr (III) from synthetic wastewater on the modified adsorbent was analysed using pseudo-first order kinetic and pseudo-second order kinetic models. The equation for both kinetic models is presented in equation (4) and (5).

\[ \log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \]  

(4)

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \]  

(5)

The pseudo-first order kinetic equation is expressed in equation (4) where \( q_e \) and \( q_t \) represent the Cr (III) uptake (mg/g) at equilibrium and at time \( t \) (min), while, \( k_1 \) (min\(^{-1}\)) is the pseudo-first order constant rate of adsorption. \( q_e \) and \( k_1 \) can be obtained from the gradient of plotting log \((q_e - q_t)\) versus time \((t)\), while, \( q_t \) is the measured of Cr (III) at time \( t \).

Pseudo-second order kinetic equation is expressed in Equation (5). In this linear equation, \( k_2 \) represent the pseudo-second order constant rate and it can be determined by the interception of plotting \( t/q_t \) versus time \((t)\).

3. Result and discussion

3.1. Effect of varied pH on adsorption

The effect of pH on the removal and adsorption capacity of Cr (III) is presented in figure 1. pH of the wastewater is one of the essential parameters that influence the adsorption of heavy metals. pH could affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [20]. Thus, the role of hydrogen ion concentration was examined on Cr (III) removal efficiency. The pH was varied from pH3 to pH7 at temperature and agitation speed of 25°C and 250 rpm respectively.

From figure 1, it can be seen that as the pH solution increasing from pH3 to pH5, Cr (III) removal also increase in linear form. The removal efficiency remained almost constant above pH5. This may be due to the formation of soluble hydroxyl complexes. The onset of metal hydrolysis and precipitation begin at pH more than 5. The hydrolysis of metal ions occurs by the replacement of metal ligands in the inner co-ordination sphere with the hydroxyl group. This replacement occurs after the removal of the outer hydration sphere of metal ions. Adsorption may not be related directly to the hydrolysis of the metal ion, but instead, outer hydration sphere that precede hydrolysis [21]. The hydrogen ion concentration increases if pH is low (below 5), thus, competitive adsorptions between H\(^+\) and Cr\(^{3+}\) result in low adsorption efficiency of Cr (III) ion.
Figure 1. Graph of Cr (III) removal (%) vs pH.

The optimum pH was at pH5 which Cr (III) removal was greater than 90% for various contact time as shown in figure 2. Increase the contact time may increase the removal of Cr (III) in synthetic industrial wastewater. The removal of Cr (III) was gradually decrease almost 60% of the removal between pH5 to pH7. Figure 2 shows that the maximum adsorption capacity of Cr (III) was in the range of 0.0018mg/g to 0.0019mg/g for various contact time that was occurred at optimum pH5. From the result, the optimum adsorption of Cr (III) was occurred at acidic condition.

Figure 2. Graph of adsorption capacity (mg/g) vs pH.

3.2. Effect of varied contact time on adsorption
Contact time is another important operational parameter that influence the efficiency of Cr (III) adsorption. Figure 3 shows Cr (III) removal efficiency as a function of contact time. As the contact time is longer, the removal efficiency is increased until it reaches its equilibrium adsorption state. Overall, starting at 60 minutes of contact time, Cr (III) removal efficiencies were greater than 90% for pH5 and pH6, and achieved more than 60% of Cr (III) removal for pH4. Whilst for pH3 and pH7 the removal of Cr (III) only take place between 20% to 40%.

Figure 3 revealed that at 60 minutes of contact time, the concentration of Cr (III) achieved 98% of removal in acidic condition of pH5. After 60 minutes of contact time, the plot of percentage removal


versus contact time was established to achieve equilibrium adsorptions and it was found that the adsorption process of the modified adsorbent was saturated. Thus the result indicates that the optimum contact time in removing Cr (III) in synthetic industrial wastewater is at 60 minutes. With these results, the highest binding sites for metal require shorter time to achieve a high Cr (III) removal efficiency.

![Graph of Cr (III) removal (%) vs contact time (min)](image1)

**Figure 3.** Graph of Cr (III) removal (%) vs contact time (min).

3.3. *Kinetic Study*

The behaviour of adsorption mechanism was analysed using pseudo-first order and pseudo-second order kinetic model as shown in figure 4 and 5 respectively.

![Graph of log (q_e - q_t) vs time (min)](image2)

**Figure 4.** Graph of log (q_e – q_t) vs time (min).
Figure 5. Graph of t/q vs time (min).

Table 1. Summary of kinetic study.

| Kinetic model | pH3     | pH4     | pH5     | pH6     | pH7     |
|---------------|---------|---------|---------|---------|---------|
| 1st order     |         |         |         |         |         |
| r²            | 0.3948  | 0.5535  | 0.6140  | 0.1131  | 0.4291  |
| k₁ (min⁻¹)    | 0.0108  | 0.0410  | 0.0373  | 0.0200  | 0.0060  |
| qₑ exp (mg/g) | 0.00062 | 0.00132 | 0.00190 | 0.00188 | 0.00069 |
| qₑ cal (mg/g) | 0.000   | 0.001   | 0.001   | 0.000   | 0.005   |
| 2nd order     |         |         |         |         |         |
| r²            | 0.8841  | 0.8992  | 0.9441  | 0.9944  | N/A     |
| k₂ (min⁻¹)    | 49.673  | 15.916  | 16.024  | 19.156  | N/A     |
| qₑ exp (mg/g) | 0.00062 | 0.00132 | 0.00190 | 0.00188 | N/A     |
| qₑ cal (mg/g) | 0.0004  | 0.0016  | 0.0018  | 0.0017  | N/A     |

Based on table 1, the removal of Cr (III) from the synthetic wastewater followed pseudo-second order kinetic model since the value of regression coefficient, r² in this model is between 0.8841 to 0.9944. The r² value for this model is higher compared to first order kinetic model. In the first order kinetic model, the value of r² is low which is only between 0.1131 to 0.6140. Thus, the model did not follow the first order kinetic model. Therefore, the adsorption of Cr (III) in synthetic wastewater using this modified adsorbent followed the second order kinetic model due to higher value of r².
4. Conclusion
As a conclusion, the modified adsorbent between coconut shell husk and limestone has a potential as adsorbent in removing Cr (III) from synthetic industrial wastewater. The percentage removal of Cr (III) from the wastewater sample increases with the lengthier contact time. The result showed that this adsorbent can removed Cr (III) up to 98% at optimum pH5 and contact time of 60 minutes using 250 rpm of agitation speed. The optimum adsorption capacity rate for the removal of Cr (III) is 0.0019 mg/g. The adsorption kinetic model is best fitted by pseudo-second-order model with correlation $r^2 = 0.94$. It can be understood that the parameters investigated significantly influenced the uptake of Cr (III) from the industrial synthetic wastewater onto the adsorbents. Therefore, the low-cost of adsorbent with good adsorption capacity might be an alternative in removing heavy metals in industrial wastewater.

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