Chitin–humic acid hybrid as adsorbent for Cr(III) in effluent of tannery wastewater treatment

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ABSTRACT

Adsorption of Cr(III) from both synthetic and real samples of tannery wastewater treatment's effluent on chitin–humic acid (chitin–HA) hybrid has been carried out. Rate constant and capacity of adsorption of Cr(III) from the synthetic sample were investigated and removal of Cr(III) from the real sample was tested at optimum medium acidity equivalent to pH 3.5. Characterization using Fourier transform infra red (FT-IR) spectroscopy revealed that both $-COO^-$ and N-acetyl originated from respectively humic acid (HA) and chitin were involved on the adsorption of Cr(III), and hence the Freundlich's multilayer and multi-energy adsorption model was more applicable to treat the adsorption data than the Langmuir's monolayer and mono-energy model. The quantification of adsorption capacity and rate constant using Freundlich isotherm model and first order adsorption reaching equilibrium yielded values of 6.84×10^{-4} mol g^{-1} (35.57 mg g^{-1}) and 1.70×10^{-2} min^{-1}, respectively. Removal test for the real wastewater treatment's effluent showed that the maximum amount of Cr(III) could be removed by 1 g of chitin–HA hybrid was 2.08×10^{-4} mol or equivalent to 10.82 mg.

1. Introduction

Chromium (Cr) is one of heavy metals which is easily bioaccumulated in biota. It exists in trivalent and hexavalent as stable oxidation states. The trivalent chromium (Cr(III)) in aqueous solution may exist as hydrated Cr(III), cationic hydroxo complexes $(Cr(OH)_n^{(3-n)+})$ ($n = 1$ or 2), neutral hydroxo complex $(Cr(OH)_3)$, and anionic hydroxo complex $(Cr(OH)_4^-)$. The hexavalent chromium (Cr(VI)) species exist in aqueous solution as oxyanionic species like chromate (CrO_4^{2-}), bichromate $(HCrO_4^-)$, and dichromate $(Cr_2O_7^{2-})$. The relative abundance of both Cr(III) and Cr(VI) in aqueous solution depends strongly on the medium acidity [1]. Although Cr(III) is known as essential micronutrient, but all Cr species may cause acute and chronic toxicity to human at high doses [2].

The pollution of Cr in the environment is strongly related with the presence of industries such as leather tanning, paper, paint, steel, and fossil fuel refinery industries [3]. Among these industries,

tannery industry is the worst with respect to its pollution in Indonesia.

Basic chromium sulfate (BCS) is the tanning agent used in Indonesia tannery industries. The current tanning technology typically results an uptake of 60–70% of Cr [4], and produces wastewater containing as high as 1500 mg dm^{-3} of Cr [5]. Many efforts to reduce the content of Cr in wastewaters of tannery industry have been afforded. At present, there are two methods of Cr recovery practiced, i.e., a method involving filtration of the waste liquor and followed by chemical treatment [6], and a method involving precipitation of Cr as $Cr(OH)_3$ by CaO, filtration, and subsequent dissolution in sulfuric acid to form solution for reuse [7]. The second method has been practiced in Indonesia, but this method still liberate the soluble Cr to the effluent at the concentration typically more than 100 mg dm^{-3}. This concentration is still much higher than the threshold concentration of 10 mg dm^{-3} as regulated by Indonesian Government for total Cr in liquid waste discharged to aquatic environment. Other methods for removal of Cr from tannery wastewater consist of ion exchange [8], membrane filtration [9], electrochemical treatment [10], and adsorption on several types of adsorbents such as biogas residual slurry [11], brown seaweed *Sargassum wightii* [12], fungal biomass of *Termitomyces clypeatus*

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[13], activated carbon, and charcoal [14]. Most of these methods and materials, especially for the ion exchange, membrane filtration, and electrochemical tretament, suffer from disadvantages such as being expensive and complicated. Therefore, there is still space for alternative method and methodology to economically remove Cr in tannery wastewater.

Our previous study has successfully immobilized humic acid (HA) on chitin and compared to chitin, this chitin–HA hybrid has better performance in removing Cu(II) [15], Ni(II) [16], and Cr(III) [17] from aqueous solution. In this study, the performance of chitin–HA hybrid is further evaluated to remove Cr(III) in real effluent of tannery wastewater treatment after performing rigorous optimization using synthetic effluent sample. The performance of the chitin–HA hybrid is evaluated based on data of capacity, energy, and rate constant of adsorption.

2. Experimental

2.1. Materials

All reagents in analytical grade, i.e. H_2SO_4, HCl, NaOH, and $Cr_2(SO_4)_3$ were obtained from Merck Co. Inc. (Germany) and used without further purification.

Chitin–HA hybrid was synthesized by reacting gelatinous chitin (40 g) in 250 cm^3 of 0.5 M HCl and HA (40 g) in 500 cm^3 of 0.5 M NaOH. The mixture was stirred continuously for 24 h and then aged for 6 h. The mixed solution was filtered, and the precipitation was washed and dried in oven at 50–60 °C. Procedure in detail has already described in our previous paper [15].

Stock solution of synthetic effluent of tannary wastewater treatment was prepared by dissolving 750 mg of $Cr_2(SO_4)_3$ in 1 dm^3 of water. Into the solution, 1 M NaOH solution was poured to give the final concentration of dissolved Cr(III) as high as 100 mg dm^{-3}. Working solution was made freshly by appropriate dilution of the stock solution.

2.2. Adsorption of Cr(III) on chitin–HA hybrid

2.2.1. Effect of medium acidity
A series of 10 cm^3 of the synthetic samples at concentration of 8 mg dm^{-3} was prepared and their acidity was adjusted to pH 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, and 7.0 by using H_2SO_4 solution. Into the solution at the respective pH, 10 mg of chitin–HA hybrid was poured and then stirred for 3 h. After filtering through 0.45-μm membrane filter, the concentrations of Cr(III) in the supernatants were analyzed by using atomic absorption spectrometry (AAS). Sample and blank solutions were analyzed under the same condition. The amount of Cr(III) sorbed was determined from the difference between the initial and remaining amounts of Cr(III) in the reacting solution after the sample was analyzed.

2.2.2. Adsorption rate
Experiments for the determination of adsorption rate were carried out using a batch-type reactor of a 25 cm^3 Erlenmeyer in a water bath at 25 ± 0.1 °C. The initial volume and Cr(III) concentration were 10 cm^3 and 8 mg dm^{-3}, respectively. To each solution, 10 mg of chitin–HA was added, the medium acidity was adjusted to pH 3.5, and stirred continuously. At selected time periods, a sample is immediately filtered through 0.45-μm membrane filter and the remaining concentration of Cr(III) in the supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under the same conditions. The amount of Cr(III) adsorbed was calculated by the difference between the initial and remaining amounts of Cr(III) in the reacting solution.

2.2.3. Capacity and energy of adsorption
Experiments for the determination of capacity and energy of adsorption were also carried out using a batch-type reactor of a 25 cm^3 Erlenmeyer in a water bath at 25 ± 0.1 °C. The effective volumes of the metal ion solutions were 10 cm^3, and the concentrations of Cr(III) in the solutions were varied from 0 to 50 mg dm^{-3}. Into each metal solution, 10 mg of chitin–HA hybrid was added and followed by continuous stirring for 3 h. After stirring, the solutions were immediately filtered through 0.45-μm membrane filter. The concentration of Cr(III) remaining in the supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under the same conditions. The amount of Cr(III) adsorbed was calculated by the difference between the initial and the remaining amounts of HA in the reacting solution. The data obtained was then analyzed using Freundlich and Langmuir iostherm models.

2.3. Application to real effluent sample

Before discarding to the environment, the wastewater of the Yogyakarta tannery industry has been treated using CaO to precipitate Cr(III) as $Cr(OH)_3$. The effluent of this treatment was collected and used as a real sample in this study. The real sample was found to still contain Cr(III) as high as 2.08×10^{-3} mol dm^{-3} or 108.15 mg dm^{-3}. Experiment with this real sample was performed using 1 g of chitin–HA hybrid and 1 dm^{-3} of diluted real samples at various dilution factors.

3. Results and discussion

3.1. Effect of medium acidity on the adsorption of Cr(III)

The adsorption of Cr(III) on chitin–HA hybrid was influenced largely by the medium acidity (Fig. 1). With decreasing medium acidity from pH 3.0 to 4.5, the adsorbed Cr(III) on chitin–HA was relatively constant, but it then decreased abruptly with the decreasing medium acidity from pH 4.5 to 7.0.

According to Sperling et al. [1], hydrated Cr(III) was the dominant Cr species at the medium acidity that was equivalent to pH 4.0 or lower, $Cr(OH)^{2+}$ was the dominant species at medium acidity between pH 4.0 and 6.5, while $Cr(OH)_3$ was the dominant species at medium acidity between pH 6.5 and 12.0. In the case of HA, it will be more negative with the decreasing medium acidity from pH 3.0 to 7.0 due to the deprotonation of especially its carboxyl groups. Accordingly it is reasonable to assume that the change of distribution of Cr species from hydrated Cr(III) to $Cr(OH)^{2+}$ and then to $Cr(OH)_3$ yielded the decrease of the amount of adsorbed Cr(III) on chitin–HA.

3.2. Adsorption rate of Cr(III)

At the optimum medium acidity (pH 3.5), the adsorption of Cr(III) on chitin–HA increased sharply from the sorption time
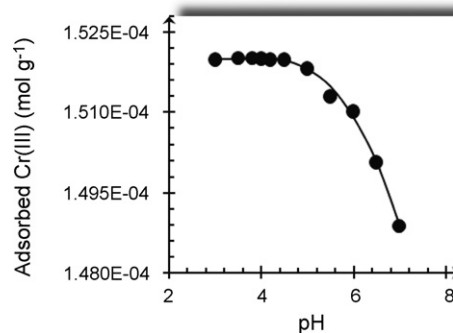

Fig. 1. Effect of medium acidity on the adsorption of Cr(III) on chitin–HA hybrid.