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Synthesis of adsorbent based on silica derived from bagasse fly ash as adsorbent chromium hexavalent in tannery waste water

RS Murti[1], NH Aprilita[2], Suyanta[2]

[1]Center for Leather, Rubber and Plastic, Yogyakarta
[2]Chemistry Department, Faculty Mathematic and Sciences, Gadjah Mada University Yogyakarta

Email: rihastiwi@gmail.com

Abstract. Adsorbent based on silica derived from bagasse fly ash has been synthesized. The synthesis adsorbent began by performing the silica synthesis of BFA by the hydrothermal alkali method. Silica gel was characterized, FTIR spectroscopy and Surface Area Analyzer. The obtained Silica was modified with Hexadeyl Tri Methyl Ammonium Bromide (HDTMAB) at concentrations of 10, 20, and 30 mmol/ L using the impregnation method. The three variations of adsorbent were applied to reduce hexavalent chromium in tannery waste water. Adsorption of chromium hexavalent were optimum at 20 mmol/L HDTMAB. The optimum adsorbent cationic was characterized using FTIR, SEM and BET spectrophotometer and applied to leather tanning waste.

1. Introduction

Leather tanning industry is an industry that in the operational use of chemicals and water in large quantities. The chromium (III) is the most popular chemical using in tannery. Chromium salts used in the tanning process. Recently, about 80-90 % of leather tanning industries using chromium salt (III). Chromium leather tanned has several advantages such as soft, heat resistant, and has a high tensile strength [1]. However, the use of chromium (III) has a negative effect because during the tanning process, chromium (III) potentially changes to chromium (VI). The chromium (VI) is highly toxic, carcinogenic and mutagenic [2]. The use of chromium in the tanning industry will cause environmental pollution if the generated waste is not maintained by appropriate methods.

Several methods have been developed to reduce Cr (VI) in water, such as electrochemical methods [3], precipitation [4] and recycle chromium from wastewater using Nano filtration membranes [5]. Those methods need skills, and a high cost in the construction, operation and maintenance. The adsorption method of Cr (VI) is relative simple, easy to do and relatively cheap. Zeolites, activated carbon, and silica gel are widely used as adsorbent material which have active sites on the surface.

Silica gel is used as adsorbent because it has stable properties under acidic conditions, non-swelling, porosity and high surface area and has a high resistance to heat [6]. Silica gel has an active site in the form of silanol (Si-OH) and siloxane groups (Si-O-Si) on its surface. Silica gel can be synthesized from siliceous materials such as quartz sand and rice husk ash. Other materials that can be used as a source of silica is bagasse fly ash / bagasse fly ash (BFA). BFA is a solid waste ash produced from burning bagasse in the sugar industry boiler. SiO_2 content is quite high and the availability of BFA abundant, can be used as an alternative material for the synthesis of silica gel.

Silica gel has an active sites silanol (Si-OH). It has a tendency to negative charged or neutral. On the other hands species Cr (VI) in the water exist in anion $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^2 which is strongly influenced by the pH of the system [7]. The use of silica adsorbent for chromium (VI) treatment have a low adsorption capacity because there is repulsion interaction between negative charge of silanol and anion Cr (VI). To increase the adsorption capacity of silica gel towards the anion Cr (VI), It is necessary to modify the silica gel to make positive charge on silica gel surface.

Modification of silica gel as adsorbent anion Cr (VI) was performed using polyaniline [8], APTMS [9], chitosan [10] and composite Hexadeyl Tri Methyl Ammonium Bromide (HDTMAB)-silica-gelatin [11]. In [12] reported that silica gel from the waste of silica industry has been modified using HDTMAB a use as adsorbent methyl orange anion. HDTMAB is a cationic surfactant which has an active group of quaternary ammonium ($-N^+{}_{R3}$) are positively charged. The aim of this research is to synthesis absorbent based on silica derived from bagasse fly ash by modification silica using HDTMAB and use this adsorbent for Cr (VI) treatment in tannery waste water.

2. Materials and Methods

2.1. Materials

The main material used in this study is silica gel obtained from BFA (bagasse fly ash) from the Sugar Factory which is located in the village Madukismo Tirtonirmolo, Kasihan, Bantul, Yogyakarta. Chemicals used in this study is the production of E. Merck, such as cetyltrimetylammonium bromide (HDTMAB), NaOH, 37 % HCl, $K_2Cr_2O_7$, acetone, H_2SO_4 1,5 - diphenyl carbazide, universal pH paper, and Whatman filter paper 42. Materials others are distilled deionized from Laboratory of PAU UGM.

2.2. Equipment

The equipment used in this study is a spectrophotometer infrared (Shimadzu FTIR-8201 PC, UV-Vis spectrophotometer (Shimadzu 1601 PC), Surface Area Analyzer (Quanta chrome 1.200e), as well as several other supporting tools such as furnace (Thermolyne Barnstead 1400), an analytical balance (Mettler Toledo A8204 S), oven (Memmert), pH meter (METLER Toledo Seven Easy), hot-plate stirrer (Thermo Scientific), shaker water bath (Kottermann), a 100-mesh sieve, and magnetic stirrer.

2.3. Methods

2.3.1. Modification of silica gel using HDTMAB

A total of 1.5 g of silica gel was dispersed into 50 ml of deionized distilled water and then added a solution of HDTMAB with various concentrations of 0; 10; 20 and 30 mmol L^{-1}. The mixture is stirred with a magnetic stirrer for 90 minutes at room temperature, and then filtered with Whatman filter paper 42 to separate the silica with the filtrate. Modified silica was washed with deionized distilled water until Cl^- free and oven-dried at a temperature of 60 ^oC for 24 hours. HDTMAB -modified silica gel is characterized by FTIR, Surface Area Analyzer and interact with a solution of Cr (VI). Furthermore, modified silica gel with HDTMAB is called SG - HDTMAB.

2.3.2. Adsorption of Cr (VI) in the leather tanning industry waste using adsorbent SG and SG-HDTMAB

Tannery waste water with certain concentration were interacted with a number of adsorbent SG and SG-HDTMAB and being shake during an hour. The mixture is then filtered using Whatman filter paper 42 and the supernatant was taken and then analyzed the levels of Cr (VI) by UV-Vis spectrophotometer. For reverence, the adsorption was also done on a standard raw material of Cr (VI) with the same condition.

2.3.3. Analysis of Cr (VI) using a UV-Vis spectrophotometer

Standard solution and the sample solution pH set it up to ± 1.25 pH by addition of a solution of 0.1 M H_2SO_4 solution was then diluted to 10 mL and 0.1 mL plus 1,5-diphenyl carbazide 0.5%. Shake and allowed to stand for 15 minutes, then measure the concentration using a UV-Vis spectrophotometer at a wavelength of 540 nm.

3. Results and Discussion

3.1. Effect of concentration of HDTMAB on Modified Silica Gel

Silanol, the functional groups on the silica gel tends to negatively charged so that it can interact electrostatically with a positively charged HDTMAB. The hydrophobic part of HDTMAB (b) interact with the other hydrophobic part of HDTMAB (b) to form a bilayer of HDTMAB on the surface of silica. The positive charge of the quaternary ammonium group ($-N^+{}_{R3}$) will interact with the anion of Cr (VI) on the adsorption process [13]. Model the interaction between SG - HDTMAB adsorbent with Cr (VI) is shown in Figure 1.

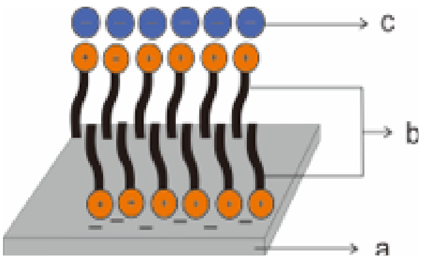

Figure 1. Interaction Model of the surface of silica gel modified HDTMAB description: Silica gel (a), HDTMAB (b), Cr (VI)

Table 1 showed the influence of concentration HDTMAB on adsorption capacity Cr (VI). The adsorption capacity increases due to the increasing of concentration HDTMAB. Based on the adsorption capability of the three variations of concentration of HDTMAB, silica gel modified using HDTMAB were optimum at 20 mmol L^{-1}. Adsorption capacity of Modified activated carbon using the HDTMAB increases due to the increasing of HDTMAB concentration [14].

Table 1. The influence of HDTMAB concentration on Cr (VI) adsorption capacity.

Adsorbent	[HDTMAB] (mmol L^{-1})	q (mg g^{-1})
SG	0	0,52
SG- HDTMAB 10	10	4,72
SG- HDTMAB 20	20	5,19
SG-HDTMAB 30	30	5,21

3.2. Characterization of adsorbent

FTIR spectra Figure 2 shows the functional groups on the silica gel and functional groups that exist on silica gel modified with HDTMAB. Sharp absorption band at wave number 3464 cm^{-1} shows the stretching vibration in silanol (Si-OH), an absorption band at 1635 cm^{-1} is a buckling of the vibration of Si-OH. The FTIR spectra of silica gel and the similarities in the results [15] and [16]. Figure 2 section b, c, and d showed the FTIR spectra of silica gel modified with HDTMAB. The appearance of an absorption band at wave number 2800-2900 cm^{-1} which indicate the presence of a methyl group (-CH_3) and methylene (-CH-) originating from the HDTMAB indicate that silica has been modified using HDTMAB.

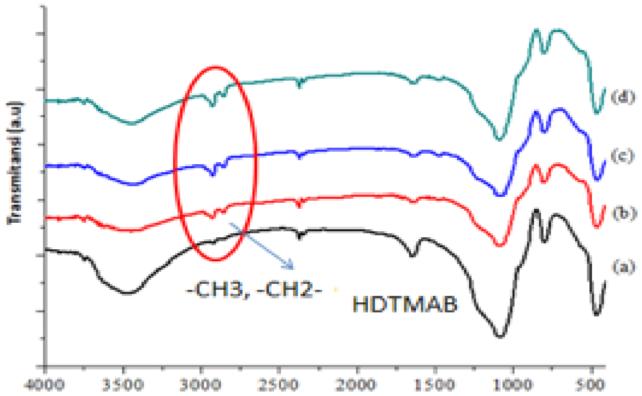

Figure 2. FTIR spectra. a) SG, b) SG-HDTMAB 10, c) SG-HDTMAB 20 d) SG-HDTMAB 30

Table 2 showed that the surface of the adsorbent properties of silica gel after being modified with HDTMAB decreased BET surface area, pore volume and pore radius. Reduced volume of pores in the silica gel - coating HDTMAB, showed that modified HDTMAB on silica gel succeed because HDTMAB filling or partially block the pores of silica gel [14], [12].

Table 2. The properties of the adsorbent surface SG and SG – HDTMAB

Parameter	Unit	SG	SG–HDTMAB
Surface area BET	$m^2 g^{-1}$	246.25	226.47
Pore volume	$ml\ g^{-1}$	0.63	0.48
Pore radius	Å	52.22	42.53

3.3. Adsorption of Cr (VI) in tannery wastewater

Comparison of the adsorption capacity of Cr(VI) in tannery waste and solution of Cr (VI) using adsorbents SG and SG-HDTMAB shown in Table 3. The ability of the adsorbent SG and SG-HDTMAB to Cr (VI) in tannery waste decreased when compared with the adsorption of Cr (VI) in the simulated waste. This is because in the tannery waste there is a lot of interference indicated by the parameters BOD, COD, TSS, TDS, Oil / fat, total Cr, Cr (VI), N-ammonia and sulfides. From the results of characterization is known that the value of Total Dissolve Solid (TDS) as high as 992 mg g^{-1}. TDS value is due in the leather tanning process receipts dissolved salts such as NaCl and Na_2SO_4. The existence of Cl^- ions and negatively charged ions SO_4^{2-} which would interfere with the process of adsorption of Cr (VI) is also negatively charged. Ion Cl^- and ion SO_4^{2-} anion will compete with Cr (VI) with active sites on the adsorbent SG and SG-HDTMAB. The competitive influence of their anion which causes a decrease in the adsorption capacity.

4. Conclusion

SG - HDTMAB adsorbent can be synthesized from silica gel obtained from BFA. The optimum concentration of HDTMAB on the modification of the silica gel reached at a concentration of 20 mmol L^{-1}. Adsorption capacity adsorbent SG - HDTMAB to Cr(VI) in tannery waste has decreased due to the effect of competitive anions such as SO_4^{2-} ions and ion Cl^-.

Table 3. Results of the adsorption of Cr (VI) using adsorbents SG and SG-HDTMAB

Adsorbent	Initial concentration (wastewater/Cr(VI) standard solution) (mg L^{-1})	Adsorption capacity Cr(VI) (mg g^{-1})	
		Cr(VI) standard solution	Wastewater
SG	25	0.82	0.25
	50	0.97	0.35
SG-HDTMAB	25	9.98	7.11
	50	12.40	9.86

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