Removal of Chromium Hexavalent Using Agriculture Waste

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Abstract—This study investigated the removal of chromium hexavalent (Cr^{6+}) using agriculture wastes. Experiments works were conducted under laboratory condition. Cr^{6+} was intensively used in industrial and manufacturing industries. Improper treatment of Cr^{6+} was lead to existing of Cr^{6+} in soil and groundwater. Tea waste (TW), coconut shell (CS) and orange peel (OP) were selected as an adsorbent to remove Cr^{6+} in this study. Characterization study on the surface morphology of TW, CS and OP was conducted using Scanning Electron Morphology (SEM), Fourier-Transfer Infrared (FTIR), and PH REdox Equilibrium (PHREEQC) software. Surface morphology of TW was significantly different compared to CS and OP. Surface morphology of TW was fully covered by wide pores and provided high reactive surface area. Surface morphology of CS and OP contained less pores compared to TW and demonstrated different type roughness. FTIR analysis revealed that TW, CS and OP contained similar chemical functional groups which were carboxyl group (C=O, C-O) and bonded-OH. Adsorption of Cr^{6+} on the surface of TW, CS and OP can be described by Freundlich isotherms. PHREEQC analysis demonstrated potential reaction mechanisms that may involve in this system were adsorption and complexation. Removal kinetics for Cr^{6+} using TW, CS and OP was measured at neutral pH under anaerobic condition using Atomic Absorption Spectroscopy (AAS). Removal of Cr^{6+} using TW was the highest compared to CS and OP in 30 mins ($k_{TW} > k_{CS} > k_{OP}$). Removal kinetic rate of Cr^{6+} using TW, CS and OP was well fitted to pseudo-first-order kinetic. This study provides significant knowledge on the potential of TW as an economic and excellent bioadsorbent for removal of heavy metals in soil and groundwater.

Index Terms—Adsorption, agriculture waste, chromium hexavalent, removal kinetic.

I. INTRODUCTION

Toxic heavy metals are abundantly present in soil and groundwater due to extensive usage of heavy metals in industrial and manufacturing activities such as smelting and mining, electroplating, leather manufacturing and tanning [1], [2]. Chromium hexavalent (Cr^{6+}) has been reported as the most predominant heavy metal found in soil and groundwater and it is very toxic and harmful to human. Previous studies have reported that Cr^{6+} caused chronic and carcinogenic diseases such as skin cancer, lung cancer and kidney damage [3]. However, fate of Cr^{6+} in soil and groundwater remained unclear.

Intensive remediation studies on the removal of heavy metals using a variety of adsorbents have been reported. For example removal of Cr^{6+} using iron-bearing soil minerals, e.g., nano zero valent iron and magnetite [4], [5] and commercial adsorbents, e.g., silica gel, activated alumina, zeolites and activated carbon [6]. These studies revealed that reactive functional groups (e.g., -OH, C=O and N-H) on the surface of adsorbents play important role on the removal of heavy metals. However, preparations of these adsorbents were complicated and adsorbent surface reactivity may decrease due to uncontrolled ions complexation with other cations [7]. Previous study also reported that an addition of chemicals (e.g., commercial polymer) into soil and groundwater may contaminate the environment [8]. Due to these limitations, agriculture waste has been used as adsorbent to remove heavy metals in soil and groundwater.

Literatures have reported that agriculture wastes (e.g., tea waste, leaves of date trees and walnut shell) were used as an adsorbent to remove heavy metals in surface water [7], [9], [10]. Recently, agriculture wastes have gain greater attention due to many obvious advantages such as easy availability, comparable efficiency, resource generation, pollution abatement, and low cost adsorbent [6], [7]. There are a lot of agriculture wastes in Malaysia such as tea waste (TW), coconut shell (CS) and orange peel (OP) that are abundantly and readily available. However, studies on the removal of heavy metals by TW, CS and OP were limited and focus only on removal rate of heavy metals. Scientific study on the potential reaction mechanisms during the removal process was not reported in detail.

In this study, we elucidated the role of agriculture wastes as an adsorbent and characterized the removal kinetic of heavy metals using agriculture wastes. TW, CS and OP were selected as an adsorbent and Cr^{6+} as a representative target heavy metal. To fulfil the goals of this study, (1) characterization study on the surface morphology of TW, CS and OP was investigated, (2) the functional groups for Cr^{6+} sorption and potential reaction mechanisms were identified and (3) removal kinetic of Cr^{6+} using TW, CS and OP were monitored.

II. PROCEDURES

A. List of Chemicals

Raw material and chemicals utilized for this study include agriculture wastes (TW, CS, and OP), Hydrochloric acid (HCl) (96%, R&M), Sodium hydroxide (NaoH) (98.86%, Fisher Scientific), and Potassium dichromate ($K_2Cr_2O_7$) (99.99%, Merck). Deaerated deionized water (DDW) prepared using ultra pure water (18Ω.cm) purged with N_2. Anaerobic chamber was maintained by purging with 95% N_2

and 5% H_2. All reagents and solutions used in the experiments were prepared using DDW.

B. Collection and Preparation of Agriculture Wastes

TW, CS and OP were selected as agriculture wastes in this study. TW was collected from the tea factory namely Boh Plantation Sdn.Bhd at Cameron Highland, Malaysia. CS and OP were collected from the Shah Alam Market, Section 16, Shah Alam. The collected wastes were washed and dried for 48 hours at 60^oC. After drying, the wastes were ground using a household simple mixer grinder to fine powder. Average size of the resulting powder was 250 μm.

C. Experimental and Analytical Procedures

All samples and experimental works were prepared and conducted under anaerobic condition. For characterization study of agriculture wastes, ground samples (1g) were transferred into amble vials (42mL) and subjected to Scanning Electron Micrographs (SEM) and Fourier-Transfer Infrared (FTIR) analysis. For adsorption experiments, 0.5, 1.0, 1.5, 2.0, 2.5, 7.0 and 10.0g of agriculture wastes were weighted and transferred into amber vials. Solution at pH 7 was prepared using 0.1 N HCl and 0.1 N NaOH. Three (3) ppm of $K_2Cr_2O_7$ was prepared with DDW containing solution at pH 7 and transferred into vials. Samples were mixed and equilibrated by a rotator for 10 mins. Concentrations of aliquots were measured using Atomic Absorption Spectroscopy (AAS). Batch experiment was performed to monitor removal kinetic of Cr^{6+} using agriculture wastes (TW, CS and OP). An approximate 0.01 g of TW, CS and OP were transferred into amble vials. Three (3) ppm of Cr^{6+} was prepared with DDW containing solution at pH 7 and poured into the vials. Samples were mixed and equilibrated by a rotator for different reaction times and the concentrations of aliquot were measured using AAS.

For characterization of agriculture waste, SEM analysis was conducted to determine the surface morphology of the TW, CS and OP. SEM was set up with LFD detection (Quanta FEG 450) with 10 kV voltage and magnification of 50,000x and 100,000x, respectively. Sample of agriculture wastes were carefully packed under anaerobic condition to avoid any reaction with oxygen. The samples were vacuumed for 5 min to avoid interference between gas molecules and electron beam, which was used for imaging to enhance resulting images. Concentration of Cr^{6+} was determined using AAS equipped with hollow cathode lamps, flame burner head and a mono-chromator. Air-acetylene flame was used at 2300^oC. Cr^{6+} can be detected at wavelength 357.9 nm. AAS was calibrated using a standard concentration of 0.1, 0.5, 1.0 and 1.5 mg/L of Cr^{6+}. The optimum detection range for this method is 0.02 mg/L to 200 mg/L.

Chemical speciation analysis of Cr^{6+} was determined using PH REdox Equilibrium (PHREEQC) software. PHREEQC is computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. It uses C and C++ programming languages that is designed to perform a wide variety of aqueous geochemical calculation. PHREEQC can be used to identify potential chemical species occur before and after reaction between surface chemical functional group on the surface of adsorbent and metals. Input data will be obtained from experimental work and FTIR analysis. Output from PHREEQC may give suggestion on the potential reaction mechanisms that occurred during adsorption process such as redox, complexation and precipitation.

III. RESULTS AND DISCUSSION

A. Characterization study of agriculture waste

Figs. 1a through 1c show the surface morphology of TW, CS and OP at neutral pH. SEM images clearly demonstrate that the surface morphology of TW, CS and OP were significantly different. Figure 1a clearly shows that TW contains large number of wide pores in its external region. Surface morphology of TW in this study was similar to surface morphology of TW collected from tea plant located in Huangshan, China [7]. Figure 1b and 1c show surface morphology of CS and OP contain fewer pores compared to TW, and surface of CS has several layers and less rough compared to OP. Literature suggests that the rough surface and widely distributed pores can offer greater surface area and more binding sites for metal [7]. This result suggests that different type of surface morphology of TW, CS and OP may significantly contribute to different removal kinetic of Cr^{6+}.
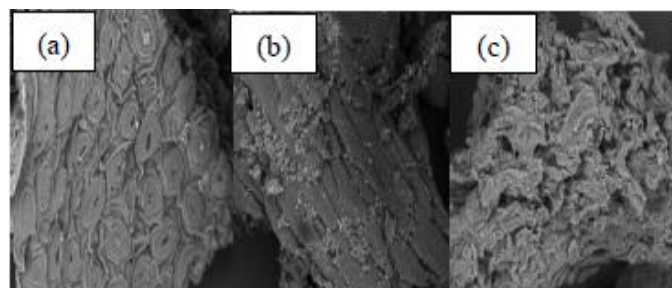

Fig. 1. SEM images of agriculture wastes at pH 7(scale : 100 μm) : (a) TW, (b) CS and (3) OP.

B. Chemical Speciation Analysis

Table I shows FTIR spectral characteristic analysis of TW, CS and OP. This analysis shows that these wastes have similar chemical functional group on their surfaces. Chemical functional group of carbon-oxygen single (C-O, carboxyl) (wavelength: 1015-1240 cm^{-1}) and oxygen hydrogen (bonded-OH, hydroxyl) (wavelength: 2500-3350 cm^{-1}) were observed on these agriculture wastes. However, chemical functional group of carbon-oxygen double (C=O; carboxyl) (wavelength 1711.14 cm^{-1}) can only be observed on the surface of CS. This result indicates that ion exchange mechanisms of C-O stretching (carboxyl), C=O stretching (carboxyl) and bonded-OH (hydroxyl) groups provide predominant sorption sites for Cr^{6+} binding. Literature suggests that ion exchange mechanisms between metal (M^{2+}) and bonded-OH (R-$(OH)_2$; R= carbon-carbon stretch) on the surface of agriculture wastes probably the main reaction mechanism because bonded-OH is a stronger nucleophile compared to carboxyl group [11]. The ion exchange mechanism between Cr^{6+} and bonded-OH can be presented as equation 1 [7], [11].
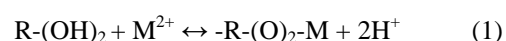
$$R\text{-}(OH)_2 + M^{2+} \leftrightarrow \text{-}R\text{-}(O)_2\text{-}M + 2H^+ \qquad (1)$$

TABLE I: FTIR SPECTRAL CHARACTERISTIC OF TW, CS AND OP BEFORE REMOVAL REACTION

| Chemical Functional groups	Standard Range of Wavelength (cm^{-1})	Actual Wavelength (cm^{-1})	Type of agriculture wastes
Carbon-oxygen single C-O	1000-1300	1028.68	TW
Oxygen hydrogen O-H	2500-3300	3250.30	TW
Carbon-oxygen single C-O	1000-1300	1031.52, 1239.42	CS
Carbon-oxygen Double C=O	1680-1750	1711.14	CS
Oxygen hydrogen O-H	2500-3350	3347.63	CS
Carbon-oxygen single C-O	1000-1300	1015.67, 1276.88	OP
Oxygen hydrogen O-H	2500-3350	3286.21	OP

Fig. 2 shows the concentration of adsorbed Cr^{6+} on the surface of TW, CS and OP at pH 7 in 10 mins. Results significantly show that TW has high capacity to adsorb Cr^{6+} compared to CS and OP. The sorption isotherm of Cr^{6+} on the surface of TW, CS and OP fitted well with Freundlich isotherm. TW has the ability to adsorb Cr^{6+} at approximately 50% more than the CS and OP, indicating that TW has greater metal-ion binding capacity compared to CS and OP. This result suggests that TW may provide higher reactive surface area to enhance ion-exchange mechanism of the hydroxyl (bonded-OH) and carboxyl groups (C=O, C-O) with Cr^{6+} compared to CS and OP. PHREEQC analysis also shows Cr6+ reaction with bonded-OH via complexation. Several chemical species of Cr^{6+} with bonded-OH were identified (e.g., $Cr(OH)_6$ and $Cr(OH)_3$). This result suggests that equation 1 significantly represent the complexation reaction mechanism and Freundlich isotherm that may be occurred in this system. Previous study has also reported that bonded-OH on the surface of TW formed complexation with copper (II) [7]. Theoretically bonded-OH is a strong nucleophile and it significantly form complexation with heavy metals [11].
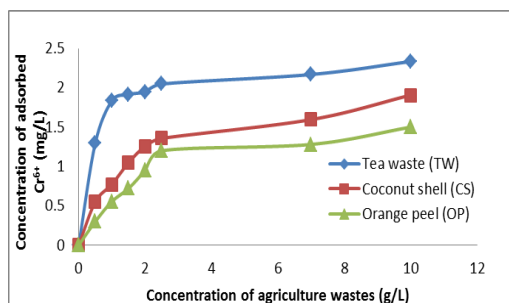
Fig. 2. Concentration of adsorbed Cr^{6+} on the surface of TW, CS and OP at pH 7.

C. Removal Kinetic of Cr^{6+} Using Agriculture Wastes

Fig. 3 shows removal kinetics of Cr^{6+} using TW, CS and OP at neutral pH under anaerobic condition. The kinetic data of Cr^{6+} removal using several agriculture wastes were fitted by a pseudo-first-order kinetic model ($R^2 = 0.97$). Removal kinetic of Cr^{6+} using TW ($k_{TW} = 0.814$ min-1) was 18 times and 10.3 times greater than that using CS ($k_{CS} = 0.045$ min^{-1}) and OP ($k_{OP} = 0.079$ min^{-1}) respectively in 30 mins. Approximately 95% of Cr^{6+} was removed by TW, while 44% and 10% of Cr^{6+} were removed by CS and OP respectively in 10 mins. Furthermore, removal kinetics of Cr^{6+} using CS and OP were slow until to the end of sampling time. Experimental results indicate that different types of agriculture wastes have significantly different kinetic reactivity as adsorbent for heavy metal removal. Based on the FTIR analysis, C-O stretching (carboxyl) and bonded-OH were present on the surface of TW, CS and OP and these chemical functional groups play significant role on the removal of Cr^{6+}. Previous study has reported that chemical functional groups such as bonded-OH and carboxyl group (C=O) were present on the surface of TW and they reacted reactively with heavy metals in aqueous phase [7]. Even though CS and OP also contained similar chemical functional groups, removal kinetic of Cr^{6+} by these agriculture wastes was significantly lower compared to removal kinetic of Cr^{6+} by TW. This is due to the unique surface morphology of TW that was rough and contained of large number of wide pores. This study provides significant evidence that surface morphology of adsorbent also plays significant role on the removal of heavy metal at neutral pH. This constitute a breakthrough on no previous reports had come to this finding.
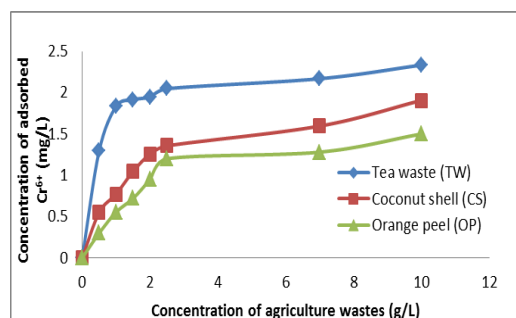
Fig. 3. Removal kinetic of Cr^{6+} by agriculture wastes. [Cr^{6+}]= 3ppm, [agriculture waste (TW, CS and OP)] = 0.01g, pH =7.

IV. CONCLUSION

This study investigated role of agriculture wastes as an effective adsorbent to remove Cr^{6+} in soil and groundwater. TW was identified as the most effective adsorbent to remove Cr^{6+} at neutral pH. Characterization study of surface of TW, CS and OP shows that TW has unique surface morphology. Surface morphology of TW was fully covered by wide pores and provided high reactive surface area to allow ion-exchange mechanism of the bonded-OH and carboxyl group (C=O, C-O) with Cr^{6+}. Surface morphology of CS and OP were rough and contain less pores. Adsorption of Cr^{6+} on the surface of TW was at approximately 50% higher compared to CS and OP in 10 mins. Adsorption of Cr^{6+} on the surface of TW, CS and OP can be described by Freundlich isotherms. PHREEQC analysis demonstrates potential reaction mechanisms that may involve in this system were adsorption and complexation. Removal kinetic of Cr^{6+} using TW was the highest compared to CS and OP in 30 mins ($k_{TW} > k_{CS} > k_{OP}$). This study also reveals that surface morphology of adsorbent plays an important role to enhance removal kinetic of Cr^{6+} even though carboxyl group (C=O,

C-O) and bonded-OH were predominant chemical functional groups that were present on the surface of TW, CS and OP. This constitutes a novel finding which has not been previously reported. This study provides significant finding on the potential natural bioadsorbent TW as a commercial adsorbent to remove heavy metal in soil and groundwater. However, further study need to be conducted to identify optimum condition to enhance removal of Cr^{6+} using TW and additional parameters (e.g., electrolytes, microorganisms, and pH) need to be investigated before real application of TW as an adsorbent at contaminated site.

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