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Polyvinyl Alcohol/Chitosan/Silicon Dioxide (PVA/CS/Sio_2) Beads For Removal Of Chromium (VI) Ions

Rizamarhaiza Muda, Syazwan Liyana Sulaiman,
*Sufizar Ahmad, and Hariati Mohd Taib**

Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, 86400, Batu Pahat,Johor ,Malaysia.

* hariati@uthm.edu.my

ABSTRACT

Chromium pollution has become a global issue and many techniques have been developed for the removal of Chromium (Cr) VI ions from wastewater. In this study, blended polymer absorbent beads which was polyvinyl alcohol/chitosan/silicon dioxide (PVA/CS/SiO_2) beads were prepared by a dropwise method by crosslinking of sodium hydroxide, ethanol and glutaraldehyde in aqueous solution. The varied concentration of CS from 0.5 to 2.5g and concentration of SiO_2 from 0 to 1.0g. All of the samples of crosslinked PVA/CS/SiO_2 beads were put under UV irradiation for two hours in Cr(VI) solution. Analyses performed on the beads were by Atomic Absorption Spectroscopy (AAS), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) analysis. Moreover, in the pH value for each sample before and after the absorption test also has been measured. Beads morphology images showed that all of the samples of PVA/CS/SiO_2 beads revealed macro and micro pores on the surface of beads before the Cr(VI) absorption and the pore size increased with the increment of CS and SiO_2 concentration. The surface of beads that became smooth after Cr(VI) absorption, indicated that the pores on the surface were filled up with Cr. This is further supported by the EDX analysis which evidently shows Cr peaks. The results of pH value of Cr after the absorption test showed that lowest pH value of 5.81 and highest pH value of 6.08. The absorption of Cr(VI) in the PVA/CS/SiO_2 beads was found to be in the range of 90% and above , as analyzed by the AAS technique. Thus it can be concluded that the use of PVA/CS/SiO_2 beads is indeed significant for eliminating Cr(VI) from industrial wastewater.

Keywords: *Polyvinyl alcohol, Silicon Dioxide, Blended polymer beads, Chromium (VI) removal*

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Introduction

Heavy metal pollution is one of the most significant environmental problems. Among various heavy metals, Chromium (VI) possess serious problem to ecosystems and causes great public concern. The sources of Cr pollutant are effluents from processes of electroplating, metal finishing, Cr mining pigments, leather tanning, wood protection, electrical and electronic equipment manufactures and catalysis [1]. Cr occurs mainly in two stable oxidation states (III) and (VI), which exhibit very different toxicities and mobilities [2].

Cr(VI) is less toxic and is an essential micronutrient for normal glucose metabolism at low concentrations. Hexavalent chromium, Cr(VI) is reported to be five hundred times more toxic than the trivalent one and is a powerful carcinogenic agent which modifies the DNA transcription process causing important chromosomal aberrations [3, 4]. The affection can be cause lung cancer, as well as kidney, liver and gastric damage [5]. The maximum concentration limit of Cr(VI) for discharge into inland surface water is 0.1 mg/L, but the guidelines for drinking water prescribed by the World Health Organization for Cr (VI) is 0.05 mg/L [6].

The issue of Cr(VI) removal from wastewater is of significant importance because of the tremendous threat of Cr(VI) contaminated wastewaters to the environment [7]. Many methods have been developed for the removal of Cr(VI) ions from wastewater, including adsorption [8], ion exchange [9], chemical precipitation [10], reverse osmosis [11], bifunctional TiO_2 catalyzed photo reduction [12] and electrolysis [13].

Absorption is one of the most popular methods for the removal of Cr (VI) from wastewaters [14]. However, most of these absorbents are either prepared in certain conditions, e.g., high temperature, controlled pressure and additional chemicals which increase operation costs or of low efficiency, poor mechanical strength and difficult separation from the reaction system. Therefore, there is a need to develop low cost, easily available, effective and reusable absorbents for the removal of heavy metal ions from the aqueous environment [15].

Polyvinyl alcohol/Chitosan (PVA/CS) pairing has gained much attention from many researchers and widely applied in a removal of heavy metal ions from aqueous solution [16]. PVA is a water soluble material containing a large amount of hydroxyl groups. PVA has been widely applied because it has many advantages such as low cost, non-toxicity, biocompatibility, high durability and chemical stability [17]. CS is just one of the most representative biopolymers, receiving considerable interest for heavy metals removal due to its excellent metal-binding capacities and low cost. CS, poly (b-1-4)-2-amino-2-deoxy-d- glucopyranose, is produced by partially alkaline N-deacetylation of chitin, which can be widely found in the exoskeleton of shellfish and crustaceans as the second most abundant natural biopolymers next to cellulose [18]. It is known as an outstanding sorbent of extremely high affinity for transition and post transition metal ions selectively because the amino (NH2) and/or hydroxy (−OH) groups on CS chains serve as coordination sites [19].

Thus, the paper highlights the fabrication of $PVA/CS/SiO_2$ beads and the capability for Cr (VI) ions removal.

Methodology

Raw Materials

Raw materials used included polyvinyl alcohol (PVA), Industrial Grade, Dngka Company), chitosan (CS, Aldrich, Alabama, USA), silicon dioxide (SiO_2), acetic acid (CH_3COOH, Qrec, Malaysia), sodium hydroxide (NaOH, EMORY, Georgia , United State), sodium sulphate (Na_2SO_4, R&M Marketing, Essex, UK) and glutaraldehyde (GLA) 50%(C_5H_8O, Alfa Aeser, Grear Britain). This study also used hydrochloric acid 37% (HCl) which was originally purchased from Qrec, Malaysia.

Preparation of PVA/CS/SiO_2 beads

The preparation of PVA/CS/SiO_2 beads were performed *via* the dropwise method where the variable involved are concentration of CS and concentration of SiO_2.

The PVA solution was prepared by dissolving the PVA in distilled water by the assistance of stirring with a mechanical stirrer and was then left overnight. CS was dissolved in 1.0 M of an acetic acid solution at different concentration of CS and stirred at room temperature. PVA/CS and SiO_2 were then mixed together and stirred until a homogeneous solution was obtained. The resulting solution was then cross-linked in 5.0 M sodium hydroxide (NaOH) solution with ethanol (95%) by a dropwise method by using a syringe and were left overnight. The beads were then rinsed with 0.5 M of sodium sulfate. The PVA/CS/SiO_2 beads are then suspended in 0.5 M of glutaraldehyde (GLA) solution and were left overnight. Finally, the beads were rinsed with distilled water to remove residual agents and kept in distilled water for further use.

Adsorption experiments

The adsorption of Cr(VI) ions was performed at pH 2. All absorption process was performed under MB-100/F SPECTROLINE MODEL ultraviolet (UV) lamp (λ=365nm) and the pH of Cr solution was pH 2 by using 20g (wet weight) of PVA/CS/SiO_2 beads. 50ml of Cr(VI) solution with the concentration of 50 ppm were placed in the same beaker. The samples were placed under UV irradiation for 2hr. The efficiency (R) of the Cr(VI) ion removal from aqueous solution (%) was calculated using the following Equation (1).

$$R= \frac{Ws-W}{W} \text{ x } 100 \qquad (1)$$

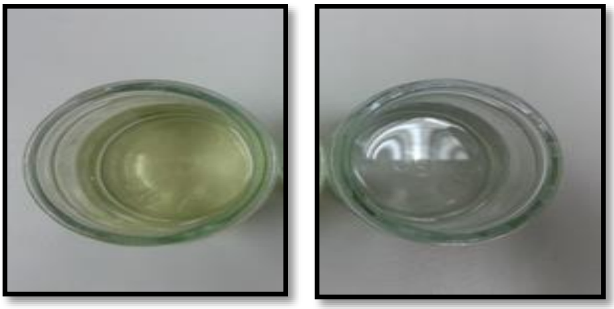
Where Ws is the weight of swollen and W for dry beads respectively.

Characterization and analyses of PVA/CS/SiO_2 beads

Beads morphology, elemental analysis and its spectrum bonding of varied concentration of CS and SiO_2 before and after the Cr(VI) absorption were performed and characterized by Scanning Electron Microscopy (SEM) analysis and Energy Dispersive X-Ray Spectroscopy Analysis (EDX) analysis. The Cr(VI) solution before and after the absorption experiment was evaluated by Atomic Absorption Spectroscopy (AAS) analysis.

Visual observation

The Cr(VI) solution shown yellow in color before the adsorption by the beads. Then, the Cr(VI) solution was changed to colorless after the treatment under UV irradiation. The reduction of Cr(VI) to Cr(III) were observed clearly by distinct color change as illustrated in Figure 1.



(a) Before adsorption (b) After adsorption

Figure 1: Chromium solution before and after absorption of PVA/CS/SiO_2 beads

This indicated that Cr(VI) has been reduced to Cr(III). The colorless solution may refer to the Cr(III) which is less harmful compared to the Cr(VI) [20].

Morphology of Beads

The surface of morphology PVA/CS/SiO_2 beads before and after Cr(VI) absorption was observed in Figure 2. The images of beads before Cr(VI) showed in Figure 2(a) which clearly shows the micro pores which were responsible for contributing to Cr (VI) absorption.

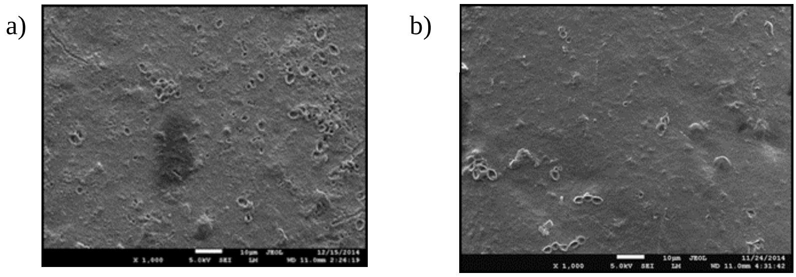


Figure 2 : Surface morphology of PVA/CS/SiO_2 beads at magnification a) 1000x (before Cr(VI) absorption) and b) 1000x (after Cr(VI) absorption)

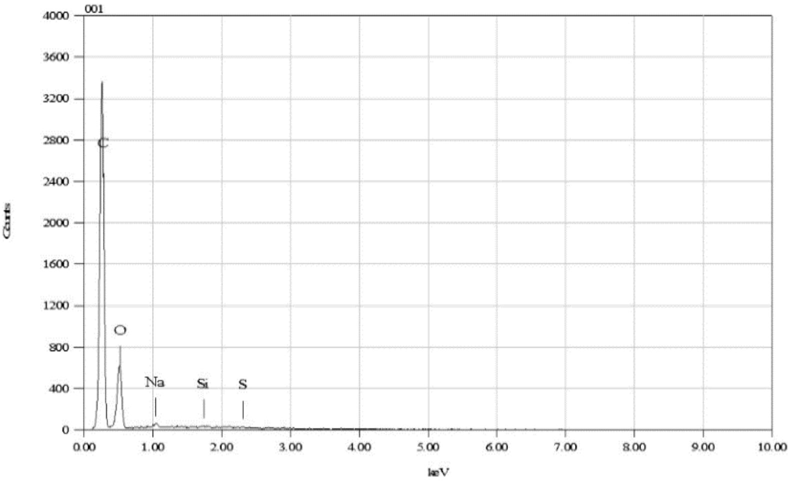
There were indeed a lot of pores on the surface before, compared to after absorption. However, the macro pores seen in Figure 2(a) were not observed as in Figure 2(b**)** it was obvious that clearly and the surface micrographs changed after Cr absorption. This is similar to observation work done by Kousalya and Hui which has been mentioned that beads showed the surface change after the absorption of Cr and phosphate [21, 22]. Figure 2(b) also clearly shows smooth surface indicating the successful absorption of Cr in the pores after absorption [22].

Elemental analysis

The identification of elements in the PVA/CS/SiO$_2$ beads and Cr(VI) absorb in PVA/CS/SiO$_2$ beads were as shown in Figure 3.

The presence of major Carbon (C), Sodium (Na), Silicon (Si), Oxygen (O) and Sulphur (S) element were observed.

a) Before adsorption Cr(VI)



b) After adsorption Cr(VI)

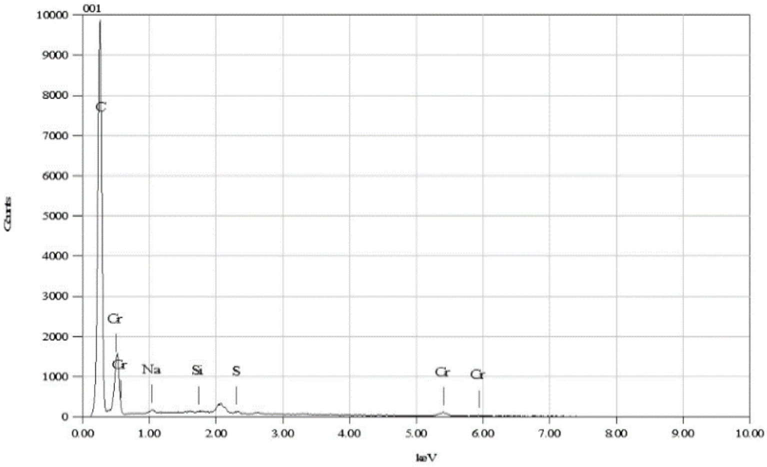


Figure 3: Representative EDX spectrum of PVA/CS/SiO$_2$ beads (a) before Cr (VI) absorption (b) after Cr (VI) absorption

Figure 3(b) showed the Cr peaks which confirm that the Cr sorption occurred onto the PVA/CS/SiO$_2$ beads. It is noted that there was no Cr peak observed in Figure 3(a).

pH Measurement for Each Sample After the Absorption Test

Table 1 shows the pH Cr(VI) solution increased after absorption test which increased of CS addition without of SiO$_2$.

Table 1: pH of Cr (VI) solution for each sample after the absorption test

pH of Cr(VI) solution after adsorption test					
SiO_2 (g) **CS (g)**	**0.00**	**0.25**	**0.50**	**0.75**	**1.00**
0.50	5.81	5.85	5.86	5.89	6.05
1.00	5.85	5.88	5.92	6.04	6.06
1.50	5.87	5.89	6.03	6.05	6.07
2.00	5.92	6.01	6.03	6.06	6.07
2.50	6.01	6.01	6.04	6.06	6.08

It is clearly that the pH of the treated Cr(VI) solution were shifted towards pH 7(neutral) when the addition of CS content increased for all types of beads, with and without SiO_2 addition.

The effects of SiO_2 addition were similar to the effects of CS addition. As the SiO_2 addition increased, the pH value also shifted towards pH 7(neutral).

This proves that increased CS assist towards better absorption of Cr(VI) ion from Cr solution by PVA/CS/SiO_2 beads, hence, the Cr solution become less hazardous and more neutral.

With the increase in pH, the degree of protonation of surface reduces gradually [24].The protonated surface becomes weaker and this led to the photocatalytic reaction to decrease and this is the reason why the absorption or photocatalytic activity was stopped at pH 5-6 [20].

Factor affecting the efficiency of Cr (VI) ions removal

Effect of CS addition on Cr (VI) absorption

Table 2 shows the percentage of absorption of Cr(VI) ions of samples with increasing CS addition.

Table 2: Percentage (%) absorption of Cr (VI) for each sample of beads

pH of Cr(VI) solution after adsorption test					
SiO_2 (g) **CS (g)**	**0.00**	**0.25**	**0.50**	**0.75**	**1.00**
0.50	93.40	94.70	95.00	96.90	99.20
1.00	94.80	96.60	97.10	98.90	99.60
1.50	95.20	96.90	98.60	99.10	99.70
2.00	97.10	98.40	98.70	99.50	99.70
2.50	98.30	98.30	98.80	99.50	99.90

Even without the addition of SiO_2, the absorption also shows increased when the addition of CS. Amino groups from CS will react with a $HCrO_4^-$ ion from Cr(VI) which called as chromate anion. With the increase of CS addition, it will increase the protonated amino groups of CS resulting in stronger electrostatic interactions between Cr(VI) anions and CS [25].

Effect of SiO_2 addtion on Cr(VI) absorption

Figure 4 shows the absorption performances of PVA/CS/SiO_2 beads added with various SiO_2 concentration. It was found that the addition of SiO_2 significantly improved the absorption performance of the PVA/CS/SiO_2 beads.

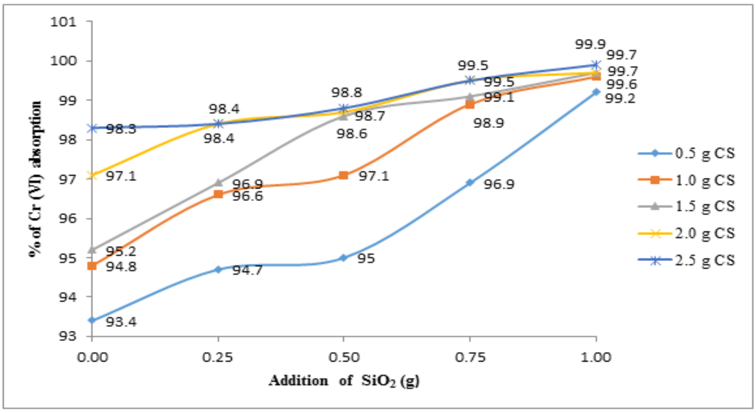


Figure 4**:** Effect of different SiO_2 addition on Cr(VI) absorption

The effect of SiO_2 was significant which was indicated by as the amount of SiO_2 increased, the absorption capability of PVA/CS/SiO_2 beads will also increase. Hence, it can be said that the SiO_2 addition also plays an important role on absorption capability of PVA/CS/SiO_2 beads. The absorption capability of PVA/CS/SiO_2 beads will be improved by using a high dosage of SiO_2.

The heavy metals absorption mechanism of PVA/CS/SiO_2 beads is related to the photocatalytic degradation process. SiO_2 which produces the electron–hole pair is responsible for the Cr(VI) reduction to Cr(III). Under exposure to the source of light, the electron (e^-) and hole (h^+) generated are capable of initiating the triple-electron reaction of Cr(VI) to stable Cr(III) [24].

Conclusion

PVA/CS/SiO_2 beads were successfully synthesized through a simple dropwise technique. A range of 0.50 to 2.50g CS and 0.25 to 1.00g SiO_2 was added to the beads .It was found the increased addition of both CS and SiO_2 were found to assist the PVA/CS/SiO_2 performance and it was successful absorbance of Cr(VI) ions as high as 99% was achieved.

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