International Journal of Integrated Engineering: Special Issue 2018: Innovations in Civil Engineering, Vol. 10 No. 9 (2018) p. 43-47
DOI: https://doi.org/10.30880/ijie.2018.10.09.008

Adsorption Efficiency of Polyvinyl Alcohol -Alginate Beads on Cr (VI): Effect of pH and Temperature

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Received 11 April 2018; accepted 19 November 2018, available online 31 December 2018

Abstract: Chromium pollution has been an increasing worldwide concern because of its high toxicity and carcinogenic properties, in which requires efficient purification technique. In the present study, adsorbent beads containing polyvinyl alcohol (PVA) and sodium alginate were prepared by crosslinked with boric acid and calcium chloride for hexavalent chromium [Cr (VI)] removal. The adsorption experiments were carried out using batch adsorption studies at various solution pH and temperatures. The results demonstrated that the optimised solution pH and temperature were observed at 1 and 70 ^{0} C, respectively. The adsorption efficiency was extremely fast and Cr (VI) was completed to be adsorbed within 45 minutes. Consequently, these results implied that the PVA-alginate beads could be considered as a potential adsorbent for Cr (VI) removal in wastewater treatment industry.

Keywords: wastewater treatment, adsorption, polyvinyl alcohol, sodium alginate, hexavalent chromium

1. Introduction

Contamination of aquatic media by heavy metals such as chromium, lead, mercury, arsenic, and cadmium has become a serious environmental issue and has raised concern in recent years. Heavy metal pollution is mainly due to the industrialisation, agricultural activities, rapid growth of world population, excessive use of chemicals, and unplanned urbanization [1]. The presence of heavy metals in natural water and industrial wastewater is a potential risk to aquatic ecosystem and public health [2].

Among all the heavy metals, chromium has received increasing worldwide attention due to its widespread applications in industrial, for instance, metallurgy, leather tanning, wood treatment, chromic salt industry, mining operation, paint processes, electroplating, and refractory materials [3]. In general, chromium exists in oxidation states ranging of -2 to +6. Among these, hexavalent chromium (VI) is the most stable form with highly toxic and carcinogenic agent owing to the existence of hydrogen chromate ($HCrO^{4-}$) and dichromate ($Cr_2O_7^{2-}$). Hence, strong exposure to Cr (VI) causes nausea, cancer in the digestive tract and lungs, as well as epigastric pain [4]. Additionally, high level of Cr (VI) in underwater sediments can lead to chromium pollution affecting fishes and benthos during anthropogenic activities, including dredging [5]. According to Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulation, the maximum permitted Cr (VI) in drinking water is 0.05 mg/L. Hence, it is necessary to perform wastewater treatment to meet the emission standard before discharge into our environment and minimise the negative impacts on ecosystem health and human health [6].

At present, numerous wastewater treatment techniques have been employed to remove Cr (VI), including chemical reduction, reverse osmosis, ion exchange, electrodialysis, and adsorption. Among them, adsorption is recognised as the most effective wastewater treatment technique for the Cr (VI) removal, with the advantages such as cost effective, various choice of adsorbent materials, and highly reusability [7]. The Cr (VI) adsorption efficiency is strongly dependent on the process parameters such as types, dosage, and size of adsorbent, temperature, solution pH, contact time, as well as types of illumination sources.

There are various types of adsorbents which have been used for heavy metals adsorption such as polyvinyl alcohol (PVA), sodium alginate [4], chitosan [3], polyvinyl chloride [8], and halloysite nanotubes (HNTs) [9]. In this study, adsorbent beads were prepared from PVA and sodium alginate. PVA is a synthetic polymer with exclusive properties such as highly soluble, non-toxicity, chemical and mechanical stability, low cost, and high diffusivity. It has been extensively used in heavy metal recovery operation and reported to be an efficient heavy metal adsorbent owing to the presence of reactive

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hydroxyl groups [7]. Meanwhile, sodium alginate is a natural biopolymer which extracted from intracellular spaces or cell walls of brown seaweed [10]. Similar to PVA, sodium alginate also possesses an excellent adsorption performances for different heavy metals [11-13]. In the present work, the PVA-alginate beads were prepared and applied for Cr (VI) removal from an aqueous solution. The effect of solution pH and temperature on Cr (VI) adsorption efficiency were investigated.

2. Methodology

2.1 Preparation of PVA-alginate Beads

12 g of PVA (Acros Organics) was added into 53 mL of distilled water and heated with a microwave at the temperature of 100 ^{o}C for 1 minute. Meanwhile, 2.5 g of sodium alginate (QRëC) was added into 20 mL of distilled water, stirring until completely dissolved. Next, the PVA gel and sodium alginate gel were mixed together with stirring until a homogenous was achieved. PVA-sodium alginate beads were produced by dropping the mixed gel with syringe needle into 6 % boric acid (QRëC) and 2 % calcium chloride which act as crosslinker. In order to allow PVA-alginate beads to cure with sufficient gelation reaction time, the beads were then kept in the crosslink solution for 24 hours. Afterwards, the beads were washed with distilled water for five times to remove the excess borate ions. Subsequently, the beads were then treated with 0.5 M sodium sulphate (QRëC) for 30 minutes to enhance its mechanical properties and chemical stability [14].

2.2 pH and Temperature Effect: Adsoprtion Studies

Firstly, the adsorption studies were performed by putting 15 g (wet weight) of PVA-alginate beads into 50 mL of 50 ppm Cr (VI) in a beaker. The initial pH of Cr (VI) solution was 5.5. Later,

i. The effect of Cr (VI) solution pH on adsorption efficiency was examined by varying the pH from 1, 3, 7, 11, to 14. The pH of Cr (VI) solution was adjusted by hydrochloric acid (QRëC, ≥ 37%) and sodium hydroxide (QRëC, Grade AR). The adsorption experiment was conducted under ultraviolet (UV) illumination at ambient temperature (24 ^{o}C). The distance between UV lamp (184 watt, 365 nm, Philips) and the beaker was maintained at 15 cm. 5 mL of sample was collected every 30 minutes during the whole period of the batch experiment and tested for Cr (VI) concentration.
ii. The effect of temperature of Cr (VI) solution on adsorption efficiency was carried out at various temperatures of 24, 40, 50, 60, and 70 ^{0} C without UV illumination. The pH of Cr (VI) was fixed at 1.5 mL of sample was collected every 15 minutes for examining the Cr (VI) concentration.

2.3 Chromium (VI) Analysis.

Diphenylcarbazide (DPC) method with a detection limit of 5 µg/L was carried out to examine the concentration of Cr (VI). 1 mL of the sample taken from each experiment was then mixed with 0.2 mL of freshly prepared 0.25% (w/v) DPC (QRëC) in acetone (Merck Schuchardt OHG), and 9 mL of 0.2 M H_2SO_4 (Merck Schuchardt OHG) in a volumetric flask. The mixture was vortexed for 15-30 seconds and allowed to stand for 10-15 minutes to achieve full colour development. The concentration of chromium (VI) was then measured by UV-Visible spectrometer (Thermo Scientific) at the wavelength of 540 nm [14,15]. Equation 1 was used to determine the Cr (VI) reduction rate of PVA-alginate beads.

$$\text{Cr (VI) adsorption (\%)} = [(C_o\text{-}C)/C_o] \times 100\ \% \quad (1)$$

C_o = initial concentration; C = final concentration

3. Results and Discussion

Figure 1 shows the Cr (VI) adsorption rate of PVA-alginate beads at various solution pH. It can be clearly seen that the adsorption efficiency of PVA-alginate beads is highly dependent on pH of the solution. The optimum pH was 1, which it only took 45 minutes to adsorb all Cr (VI) in aqueous solution. With continued increasing of pH to 3, 5.5, and 7, Cr (VI) was completely removed from the aqueous solution after 1, 1.5, and 2.5 hours, respectively. By increasing pH to alkaline level, a drastic decrease in adsorption efficiency was observed. After 3 hours of UV illumination time, the Cr (VI) adsorption rate were only 45 % and 24 % at pH of 11 and 14, respectively. Thus, it could be drawn that the Cr (VI) adsorption efficiency of PVA-alginate beads declined markedly as pH increased.

It is evident that solution pH is one of the significant parameters that affects the Cr (VI) adsorption efficiency owing to the prepared solution pH has strong influence on the chemical structure and speciation of Cr (VI). In general, Cr (VI) exists in several forms of oxyanions such as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), chromic acid ($HCrO_4^-$), and chromium trioxide (CrO_3). When the Cr (VI) solution in acidic condition, oxyanion $HCrO_4^-$ appeared as the predominant species and exists as a strong negative charged anion. On the other hand, oxyanion CrO_4^{2-} and $Cr_2O_7^{2-}$ appeared as the predominant species in alkaline Cr (VI) solution [1]. At acidic pH, the surface of PVA alginate beads tend to protonate to a greater extend during the adsorption process. As a result, the surface of beads exhibits stronger attraction for negatively charged oxyanion such as $HCrO_4^-$ from Cr (VI) and consequently promote the adsorption efficiency. Conversely, at alkaline pH, the degree of protonation of the surface was decreased and resulted to weakening of electrostatic force of attraction between adsorbate and adsorbent. Thus, it leads to the reduction of adsorption efficiency [2]. Similar results were also obtained by other researchers [14-15].

Figure 2 shows the Cr (VI) adsorption rate of PVA-alginate beads at various temperatures. It could be inferred that the adsorption efficiency of PVA-alginate

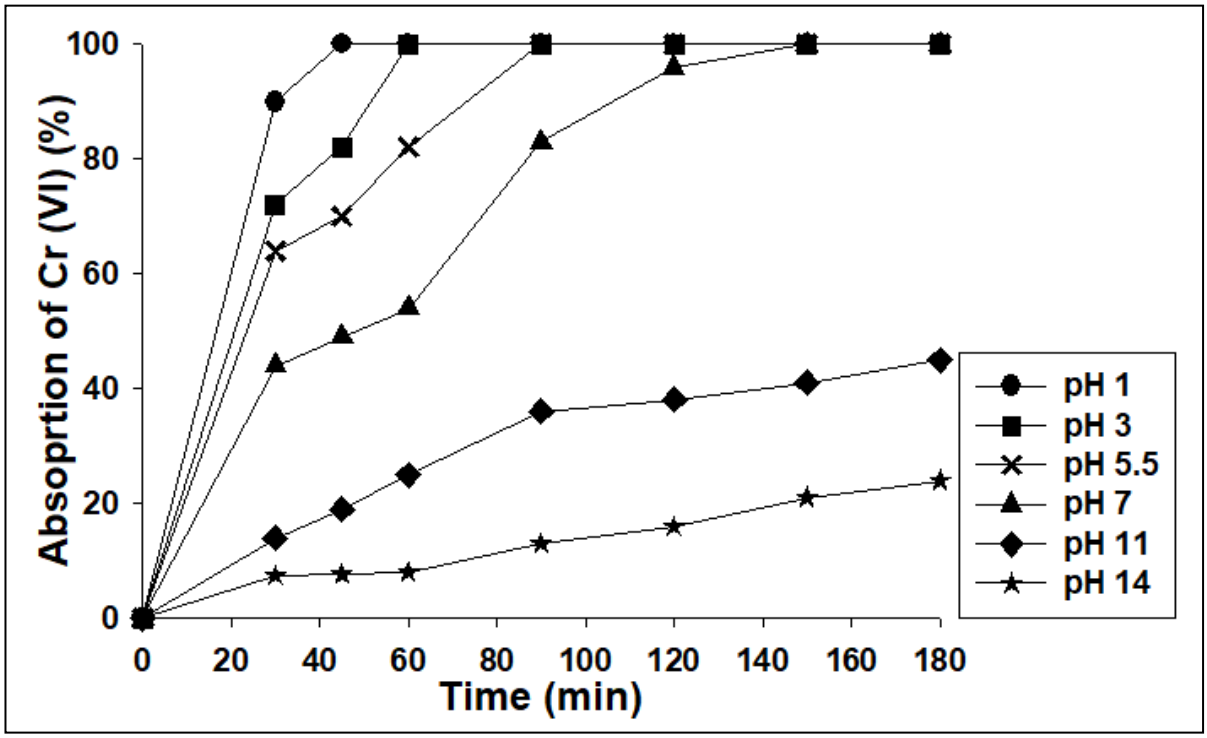

Figure 1: Effect of solution pH on the Cr (VI) removal rate with PVA-alginate beads.

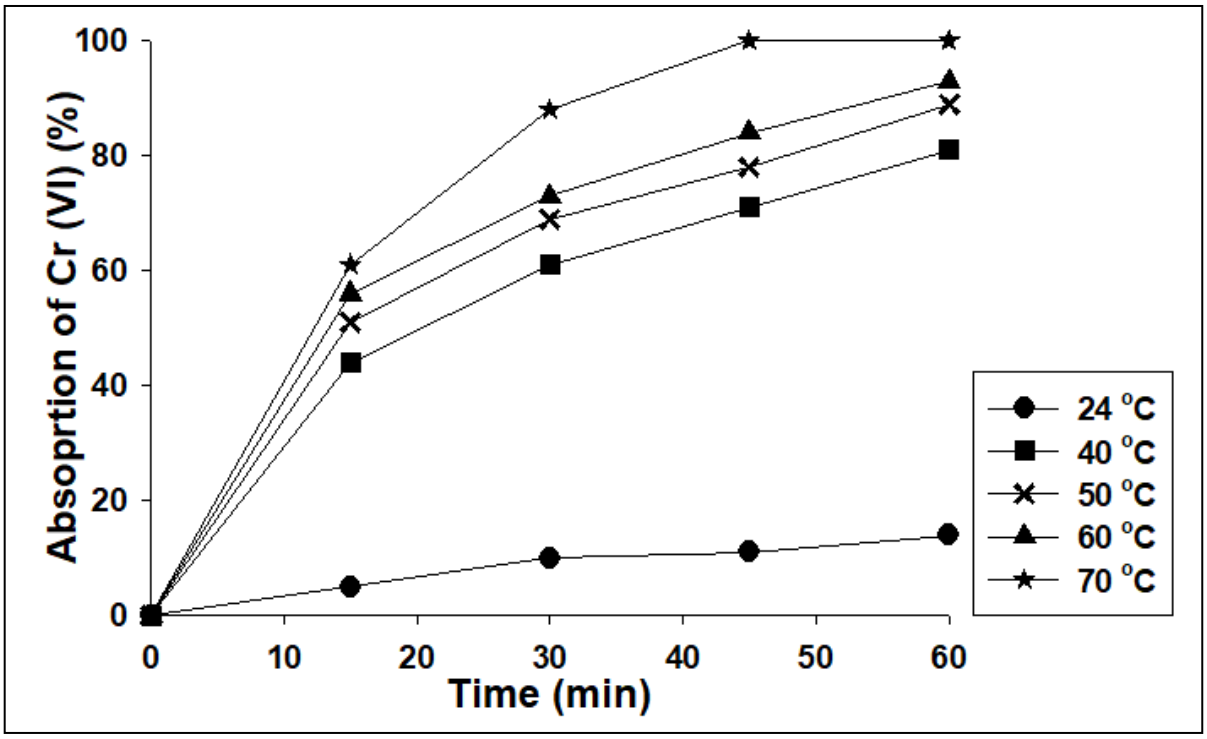

Figure 2: Effect of temperature on the Cr (VI) removal rate with PVA-alginate beads.

beads increased with increasing temperature. At temperature of 24 ^{0}C, adsorption efficiency was relatively low, as only 14 % of Cr (VI) was adsorbed by beads. On the other hand, when the temperature rose 40 ^{o}C, there was a significant rise in the adsorption efficiency of beads, 81 % of Cr (VI) was adsorbed within 1 hour. A slight change in adsorption efficiency was observed at temperature of 50 ^{0} C and 60 ^{0} C, adsorption efficiency increased to 89 % and 93 %, respectively. It can be observed that the optimum temperature was 70 ^{0} C, Cr (VI) was completely removed from the aqueous solution after 45 minutes. It is necessary to report that this study did not further increase the temperature more than 70 ^{o}C, because higher temperature leads to physical and chemical instability. As a result, the PVA-alginate beads lost its adsorption capability.

There are several viewpoints regarding the effect of temperature on polymer adsorbent. It can be classified into three, which are as follows (i) Heavy metal adsorption is an exothermic process, whereby the adsorption efficiency decreased gradually as temperature increased. (ii) Heavy metal adsorption is an endothermic process, whereby the adsorption efficiency increased gradually as temperature increased. (iii) Heavy metals adsorption does not have significant relationship with temperature [1,4]. It can be clearly seen that the adsorption efficiency of PVA-alginate beads is favoured in the high temperature for this study. Hence, it could be inferred that Cr (VI) adsorption of PVA-alginate beads is an endothermic process. The adsorption efficiency increased at higher temperature owing to the mechanisms as follows: (i) At higher temperature, the molecular movement of beads was increased due to the increasing of kinetic energy. Hence, it leads to the increasing of collision frequency between sorbent and sorbate and ultimately promotes the Cr (VI) adsorption efficiency. (ii) greater area of active sites and possible sites were formed on PVA-alginate beads at higher temperature owing to the enhancement of protonation and deprotonation of functional groups on the surface of beads, and (iii) desorption and dechelation were occurred at higher temperature and enhance the adsorption efficiency [5].

Moreover, a rapid metal uptake rate was observed after the first 30 minutes, or known as the first stage of heavy metal adsorption. The adsorption behaviour is mainly due to the abundant active sites initially available on the adsorbent surface. Afterwards, the metal adsorption rate was followed by a slower metal uptake rate until a stable equilibrium was achieved and was spread over a considerably lower period of time, which was known as the second stage of heavy metal adsorption. In this stage, adsorption occurred less efficiently due to the gradual occupancy of active site [16]. This type of adsorption pattern was observed in several studies done by others researchers on various heavy metals or adsorbents [17-19].

It is noteworthy to mention that, although the optimum removal efficiency or Cr (VI) achieved at pH 1 and 70 ^{0} C, the results also showed good and acceptable removal efficiency at pH 7 and ambient temperature as shown in Figure 1. It is not suggested that treating waste water with high acidic and temperature condition as it will be costly due to the high amount of chemical for pH adjustment and temperature increment.

4. Conclusions

The removal of Cr (VI) using PVA-alginate beads was investigated as a function of the different solution pH and temperatures. The results demonstrated that the optimum solution pH and temperature were 1 and 70 ^{0} C, as Cr (VI) was completely adsorbed by PVA-alginate beads within 45 minutes. However, the results also showed good and acceptable removal efficiency at pH 7 and ambient temperature which is able to reduce the treatment cost. Thus, it could be concluded that PVA-alginate beads demonstrated the potential in the treatment of wastewater containing Cr (VI). It is suggests that, further research should be taken to improve the adsorption capacity and apply in large-scale operations.

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