The Effects of Various Parameters on Cr (VI) Adsorption by Raw Rice Husk

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ABSTRACT   The effects of pH, contact time and adsorbent concentration on the adsorption of Cr (VI) onto raw rice husk have been investigated. The parameters - raw rice husk (RRW) particle size which was in the range of 450-600 μm, concentration from 10g/l to 70g/l, contact time 0.5 to 2.0 hours, and pH 1-8 were tested using 50mg/l solutions of Cr (VI). The maximum removal efficiency was 66.6% for RRW concentration of 70g/l, at pH 2 and 2 hours contact time. In terms of adsorption capacity, the 10g/l adsorbent concentration gave the highest reading of 2.2 mg/g for a pH of 2 and 2 hours contact time.

ABSTRAK   Kesan pH, masa sentuhan dan kepekatan penjerap terhadap penjerapan Cr (VI) ke atas sekam padi mentah telah dikaji. Parameternya – saiz zarah sekam padi mentah dalam julat 450 – 600 μm, kepekatan dari 10g/l ke 70g/l, masa sentuhan 0.5 ke 2.0 jam, dan pH 1-8 telah dikaji menggunakan 50mg/l larutan Cr (VI). Kecekapan penyingkiran maksimum adalah 66.6% bagi kepekatan sekam padi mentah 70g/l, pH 2, dan masa sentuhan 2 jam. Dari segi kapasiti penjerapan, kepekatan penjerap 10g/l memberikan bacaan tertinggi 2.2 mg/g untuk pH 2 dan masa sentuhan 2 jam.

(Adsorption, raw rice husk, concentration effect, pH effect, contact time)

INTRODUCTION

Water scarcity and degradation are growing concerns for countries around the world, and global demand for fresh water is doubling every 21 years according to the Food and Agriculture Organization (FAO). Across the world today renewable water resources available per person are roughly half what they were in 1960 and this figure is expected to drop by half again by the year 2025 according to the estimates from the World Bank [1]. Chromium is a priority metal pollutant introduced into the water bodies from many industrial processes such as tanning, electroplating, metal processing, paint manufacturing, steel fabrication and agricultural runoff [2]. Strong exposure of Cr (VI) causes cancer in the digestive tract and lungs, and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [3].

Stricter environmental regulations related to the discharge of heavy metals make it necessary to develop processes for their removal from wastewater [4]. Different alternatives for treating effluent are described in the literature, including chemical precipitation, carbon adsorption, ion exchange, and membrane separation process, among others [5]. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste streams and the activated carbon has been widely used as an adsorbent [6]. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Certainly, improved sorption capacity may compensate the cost of additional processing [7].

Rice husk, a by-product of the rice milling industry, accounts for about 20% of whole rice. With the estimated annual rice production of 500

million tones in developing countries, approximately 100 million tones of rice husk is available annually for utilization in these countries alone [8]. The cell walls of rice husk consist mainly of cellulose, silica, lignin, carbohydrates and having a lots of hydroxyl group in their structures, and the exchange properties of the husks are due to the presence of their various functional groups [9]. In the current study, the RRH was chosen as low cost adsorbent due to the fact that it requires little processing, is abundantly available locally in developing countries like Malaysia and it is a waste by-product of the rice milling industry. Batch mode study was carried out to assess the performance evaluation of raw rice husk (RRH) for the removal of Cr (VI) from wastewater.

EXPERIMENTAL

Preparation of Raw Rice Husk (RRH) as Adsorbent

Rice husk was obtained from a rice mill at Tanjong Karang, Selangor. The rice husk was washed using distilled water a few times. Washed rice husk was spread and dried in a drying oven at 100 °C for 24 hours. The dried rice husk was then sieved into the size range of 450 – 600 μm. It was then kept in an airtight container to protect from humidity.

Preparation of Simulated Wastewater

All reagents employed in this work were of analytical reagent grade. Cr (VI) stock solution with 1000 mg/l concentration was prepared by diluting 2.828 g of potassium dichromate in 1 litre of distilled water. All the working solutions were prepared by diluting the stock solution with distilled water. The pH of the wastewater was adjusted using reagent grade dilute sulfuric acid and sodium hydroxide solutions.

Batch Mode Adsorption Studies

The adsorption studies were carried out at room temperature (26 ± 1°C); 50 ml of the Cr (VI) solution with 50 mg/l concentration was treated with different concentrations of RRH (10, 20, 30, 40, 50, 60 and 70 g/l) at varying contact time (0.5, 1.0 and 2.0 hours) for different pH (1, 2, 3, 4, 5, 6, 7, and 8). The mixture was filled in a 100ml conical flask and covered with parafilm (to prevent contamination of the solution during preparation and throughout the preferred contact time). It was agitated at 200 rpm using a mechanical shaker. The reaction mixture was then filtered (using Schleicher & Schuell filter paper with pore size 45 micron) and the filtrate was analyzed for the final concentration of Cr (VI) ions (using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), model, Perkin Elmer Optima 3000). The amount of Cr (VI) adsorbed was determined by subtracting the final concentration (C_e) from the initial concentration (C_o).

The Cr (VI) removal efficiency (%) through the batch mode study was calculated using equation 1 (Eq. 1). The adsorption capacity, or mg of Cr (VI) ions adsorbed from the synthetic wastewater per g adsorbent, was calculated using equation 2 (Eq. 2).

$$\text{Cr (VI) removal efficiency} = \frac{C_o - C_e}{C_o} \times 100\% \qquad \text{(Eq. 1)}$$

$$\text{Cr (VI) adsorption capacity (mg/g)} = \frac{C_o - C_e}{m} \times V \qquad \text{(Eq. 2)}$$

where,
C_o = initial concentration of Cr (VI), mg/l
C_e = final concentration of Cr (VI), mg/l
V = total solution volume (l)
m = weight of the adsorbent (g)

RESULTS AND DISCUSSION

The Effect of pH

The effect of pH shown in Figure 1 indicates maximum removal efficiency at pH 2 (66.6 %) for contact time and adsorbent concentration of 2 hours and 70 g/l, respectively. The contact time and adsorbent concentration are both the highest used in this work. The Cr (VI) removal efficiency increased from pH 1 (40.12 %) to pH 2 (66.6 %), beyond which it decreased sharply at pH 3 (17.99 %) and continued to decrease gradually at pH 4, before leveling off to 8.29% at pH 8. Similar trends were observed when different adsorbent concentrations were used.
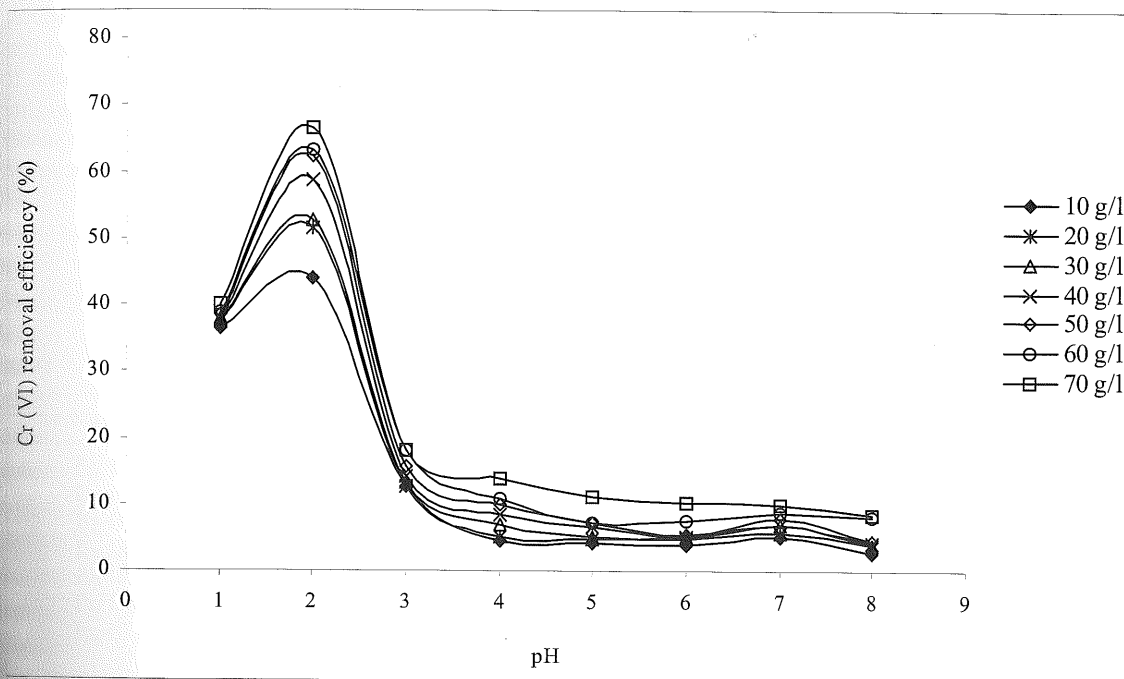

Figure 1.   Cr (VI) removal efficiency versus pH at varying adsorbent dose
[Contact time: 2 hours, Adsorbent size: 450 – 600 μm, Temperature: 26 ± 1°C, Agitation rate: 200 rpm, and Initial concentration of Cr (VI): 50mg/l]

Figure 2 shows the RRH adsorption capacity of Cr (VI) at increasing pH and adsorbent concentration. On the contrary to the removal efficiency for which the highest efficiency occurred at the highest concentration of 70g/l, the highest adsorption capacity was observed at the lowest adsorbent concentration of 10 g/l. This was observed for the entire pH range of 1 to 8. Hence, the ratio of adsorbed Cr (VI) to the mass of the adsorbent gave the highest value with the lowest adsorbent concentration (i.e. 10 g/l). The maximum removal capacity was also obtained at pH 2 (2.2 mg/g) for contact time of 2 hours. In addition as expected, all the curves of the adsorption capacity show a similar trend to the removal efficiency plots, with the removal capacity increasing between pH 1 to pH 2, followed by a sharp decrease at pH 3 and then continual decrease before leveling off around pH 5.

Both the removal efficiency and adsorption capacity show that pH 2 is the optimum pH for removal of Cr (VI) by RRH. This result is in agreement with the report [10] that maximum adsorption of Cr (VI) occurred between pH 1.5 and 2 for raw rice bran. It is possible that at this pH, there is presence of an optimal number of H^+ ions, which in turn neutralize the negatively charged adsorbent surface thereby reducing hindrance to the diffusion of dichromate ions.

The Effect of Adsorbent Concentration

The above results on pH effect have indicated that the highest adsorbent concentration leads to the highest removal efficiency while the lowest adsorbent concentration gives the best adsorption

capacity. These effects are more clearly shown in Figures 3 and 4.

For removal efficiency (Figure 3), increasing efficiency (at pH higher than 1) was obtained from adsorbent concentration of 10 to 70 g/l, as indicated previously. The maximum removal was 66.6 % occurred at for pH 2, contact time of 2 hours and adsorbent concentration of 70 g/l. The increasing removal efficiency with the increase in adsorbent concentration can be attributed to the availability of greater adsorbent surface area. On the other hand, in the case of adsorption capacity, decreasing capacity was observed with the increase of adsorbent concentration (10 to 70 g/l) at all pH. The maximum adsorption capacity was observed at pH 2 (2.2 mg/g) for adsorbent dose of 10 g/l and contact time of 2 hours. Since the adsorbate concentration was kept constant at 50 mg/l, higher concentration of adsorbents means the adsorbate are more distributed among the particles, hence each unit mass of particle has less Cr (VI) adsorbed to it. This observation implies that at lower adsorbents concentrations the particles are better utilized for adsorption compared to higher adsorbent concentrations. The low concentration, however, means less adsorbent particles which are less sufficient to remove the 50g/ml adsorbate compared to higher adsorbent concentrations, hence the lower removal efficiency.
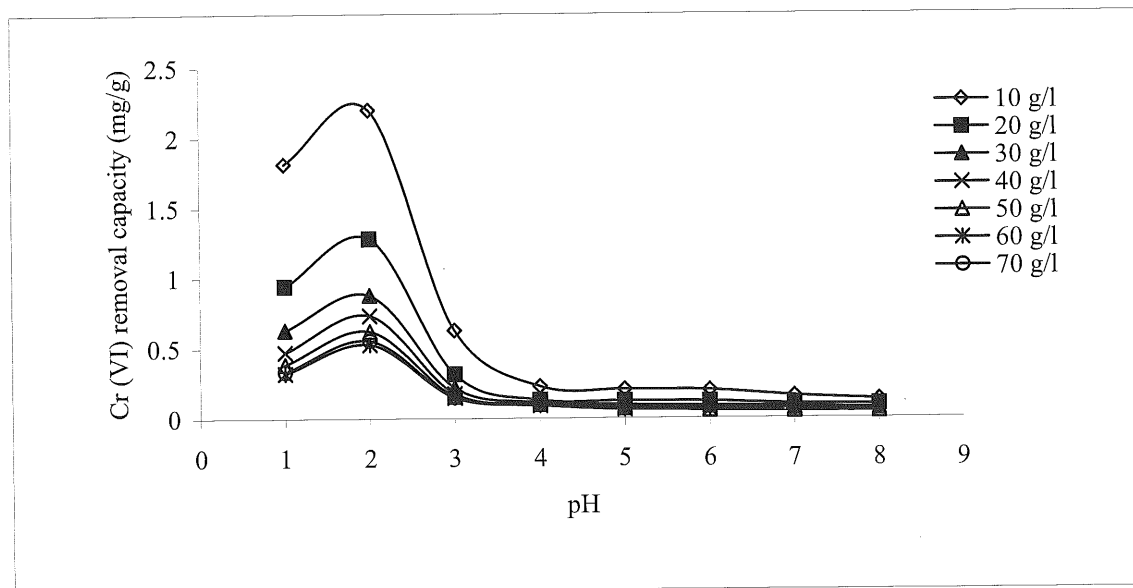

Figure 2.　Cr (VI) removal capacity versus pH at varying adsorbent dose
[Contact time: 2 hours, Adsorbent size: 450 – 600 μm, Temperature: 26 ± 1°C, Agitation rate: 200 rpm, and Initial concentration of Cr (VI): 50mg/l]
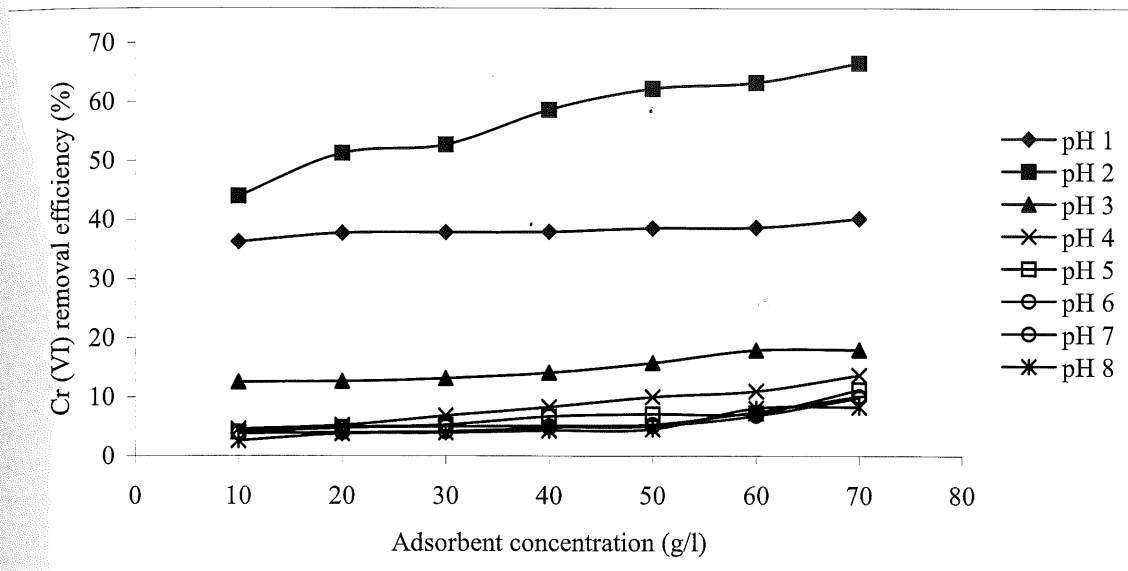
Figure 3. Cr (VI) removal efficiency versus adsorbent dose (g/l) at varying pH
[Contact time: 2 hours, Adsorbent size: 450 – 600 μm, Temperature: 26 ± 1°C, Agitation rate: 200 rpm, and Initial concentration of Cr (VI): 50mg/l]
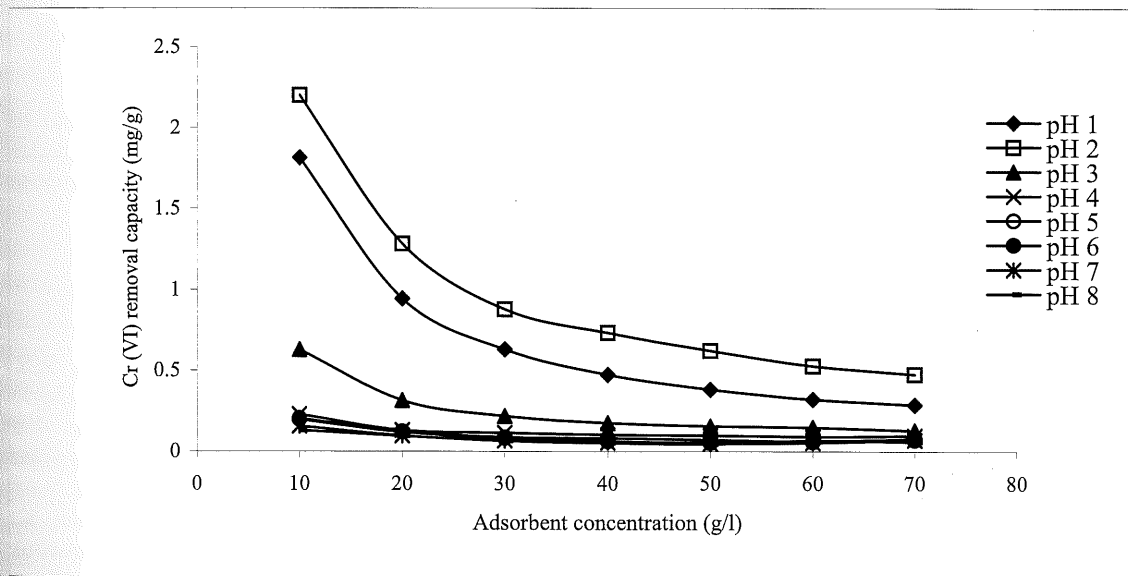

Figure 4. Cr (VI) removal capacity versus adsorbent dose (g/l) at varying pH
[Contact time: 2 hours, Adsorbent size: 450 – 600 μm, Temperature: 26 ± 1°C, Agitation rate: 200 rpm, and Initial concentration of Cr (VI): 50mg/l]
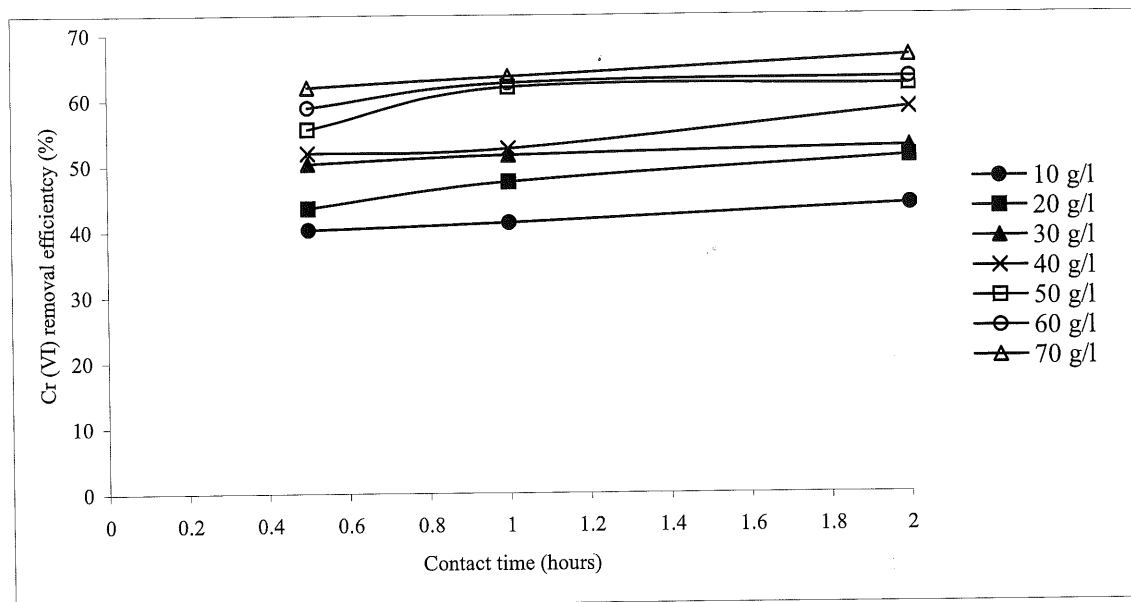
The Effect of Contact Time

Figure 5. Cr (VI) removal efficiency versus contact time (hr) at varying adsorbent dose
[pH: 2, Adsorbent size: 450 – 600 μm, Temperature: 26 ± 1°C, Agitation rate: 200 rpm, and Initial concentration of Cr (VI): 50mg/l]

The study on Cr (VI) adsorption was done at contact times of 0.5, 1.0, and 2.0 hours, with increasing removal from 0.5 hr to 2.0 hours at all adsorbent concentrations at pH 2, as shown in Figure 5. Similar trends were also observed at other pH conditions. The removal efficiency was recorded as 61.91 %, 63.55 % and 66.6 %, for contact time of 0.5, 1 and 2 hours respectively at pH 2 and adsorbent dose of 70 g/l. Removal efficiency of Cr (VI) was maximum (66.6%) at pH 2 and contact time 2 hours. The increasing efficiency is attributed to the increase in time given for the adsorbent and adsorbate to interact with each other. Contact time greater than 2 hours could lead to better removal efficiencies, until an equilibrium is achieved.

CONCLUSION

Based on the experimental conditions of this project, it can be concluded that the maximum removal efficiency of 66.6% and adsorption capacity of 2.2mg/g occurred at pH 2 for contact time of 2 hours. The highest adsorbent concentration of 70mg/l gave the best removal efficiency while the lowest adsorbent concentration of 10mg/l recorded the highest adsorption capacity. The results obtained are, however, limited to the condition of the

experiments. Further work would be useful to ascertain the optimal conditions given a wider range of parameters such as adsorbate concentrations and time of contact.

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