Modified brick powder and its adsorption performance for uranium (VI)

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ABSTRACT

Adsorption of radionuclides by adsorbent is a promising and effective method for the remediation of radioactive wastewater. A new adsorbent of modified brick powder was prepared by alkali modification. The optimum modified conditions, 15 g of brick powder (140 mesh) were added to 2 mol/L of sodium hydroxide solution, the reaction time was 12 h and the solid-liquid ratio was 1:4. In addition, different influence factors on uranium adsorption efficiency were also investigated. The results showed that the removal efficiency reached 95.28% at the initial concentration of 10 mg L^{-1}, pH 4, adsorption time of 180 min, and adsorbent dosage of 0.4 g. It was determined from regeneration experiments that the modified brick powder exhibited high sorption of U(VI) (89.66%) over four cycles. Therefore, the modified brick powder can be a promising candidate for the removal of U(VI) from aqueous solution due to its low cost, sustainable, and efficient feature.

Keywords: Clay brick powder; Sodium hydroxide modification; Uranium (VI); Adsorbent

1. Introduction

With the rapid development of the uranium mining industry, a large amount of wastewater containing uranium has been discharged into the environment [1]. The soluble $U^{(VI)}O_2^{2+}$ is easily diffused and migrated towards groundwater, which poses a potential threat to the bio-availability and human health [2]. In particular, uranium can cause damage to human biological functions such as brain, kidney and DNA structure of organisms [3,4]. Therefore, it is imperative to remove and recover the uranium from the aqueous solutions, not only for the remediation of the environment and the health of the human beings but also for the development of nuclear energy [1].

In the past decade, various processes such as chemical precipitation, ion exchange, membrane filtration, and adsorption have been employed to remove metal pollutants from aqueous solutions [5–9]. However, most of these methods are either ineffective, costly, complicated, or have toxic sludge generation problems [10]. As a result, there is a need for innovative adsorbents that are both cheap and efficient.

Waste bricks are one of the by-products of urbanization. In recent years, with the acceleration of China's urbanization process and the large-scale development of urban construction, the emission of construction waste (including a large number of waste bricks) has soared, accounting for more than 30% of the total urban waste [11]. A large number of construction waste without any treatment will be transported to the outskirts of the open air pile or landfill, causing serious environmental pollution. The utilization of waste materials can be realized by modifying waste bricks into adsorbent, protect the ecological environment, has important social significance. The modified brick powder can be

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used to remove cyanobacterial blooms [12,13]. Since chemical modifications are known to improve the characteristics of the adsorbents; therefore, in the present research, sodium hydroxide is employed to modify construction garbage of clay brick to improve its uranium (VI) adsorption efficiency for the first time.

2. Materials and methods

2.1. Adsorbent preparation

Clay brick, collected from a demolition site of Hengyang city, was washed with distilled water so as to remove dust, and then dried in the oven. After drying, the brick was weighed and powdered to obtain a 20–200 mesh size.

The specific preparation process for the sodium hydroxide–modified clay brick powder was as follows. Initially, 0.5–3.0 mol/L of the sodium hydroxide solution was prepared, and the clay brick powder was slowly added to the solution. Then, the mixed suspension was slowly stirred for 2–24 h with a constant temperature vibrator at 25°C. Finally, the suspension was filtered through a qualitative filter paper (10–15 μm), and the residue was washed to neutral with distilled water and then dried for 6 h in an oven at 40°C. The dried filter residue served as the final sodium hydroxide–modified, clay brick powder adsorbent.

2.2. Adsorption experiments

The experiment was carried out in a 250 mL Erlenmeyer flask containing modified brick powder adsorbent and 25 mL uranium solution at initial concentrations 10 mg/L and then sealed after adjusting the pH. The flask was stirred on a shaker at 200 rpm and 25°C. When the reaction was complete, the sample was filtered, and the residual uranium concentration in the filtrate was measured.

The uranium (VI) concentration was determined with the spectrophotometric method. Visible/ultraviolet spectrophotometer (722N) was acquired from Inesa Analytical Instrument Co. Ltd., (Shanghai China).

Removal efficiency (η%) was calculated using the following relationships:

$$\eta\% = \frac{C_0 - C_e}{C_0} \times 100\%$$

where C_0 and C_e represent the initial and final uranium (VI) concentration (mg/L).

2.3. Desorption

0.4 g adsorbent was added into 250 mL Erlenmeyer flask containing 25 mL of 10 mg L^{-1} uranium (VI) solution at pH 4, 25°C, and 200 rpm for 180 min, then the absorbents were recovered for desorption experiment, which was carried out with 25 mL of 0.05-M HNO$_3$ at 175 rpm and room temperature for 120 min. The absorbents–desorption cycles were repeated four times under the same conditions. The residual uranium (VI) concentration was measured by spectrophotometric method.

3. Results and discussion

3.1. Effect of sodium hydroxide concentration

Sodium hydroxide or calcium hydroxide are often used as a modifier to prepare adsorbent for treating metal ions or algae [14–16]. In the current work, in order to investigate the effect of sodium hydroxide concentration on uranium adsorption of modified fly ash brick powder, the following experiments were carried out, the results are shown in Fig. 1. The removal efficiency of uranium (VI) increases significantly from 62.51% with a 0.5 mol/L sodium hydroxide concentration to 90.53% with concentrations greater than 2 mol/L. Therefore, the present study suggests that optimal uranium (VI) removal may be achieved with sodium hydroxide concentration of 2 mol/L. Sodium hydroxide modification might enhance physical adsorption by enlarging surface area and pore volume as well as chemical adsorption by increasing ion exchange and forming crystalline species demonstrated by microscopy (SEM-EDX) and X-ray diffraction analysis [15].

3.2. Effect of the modified time

The influence of modification time on the removal efficiency is shown in Fig. 2. It could be seen that a modification in time can effectively increase the removal efficiency of uranium (VI). The removal efficiency of uranium (VI) increased initially from 35.77% with a 2 h modified time to 92.03% with times greater than 12 h, and then extremely slow increased with the increase of time. Therefore, the optimum modified time was 12 h. Wang [17] thought that with the increase of modification time, the modifier reacted with the adsorption group on the surface of adsorbent to make the inactive adsorption point active. As an activation process, the removal rate increased with the increase of modification time.

3.3. Effect of solid to liquid ratio

The removal efficiency of U (VI) at different solid to liquid ratio is presented in Fig. 3. As shown in the figure,
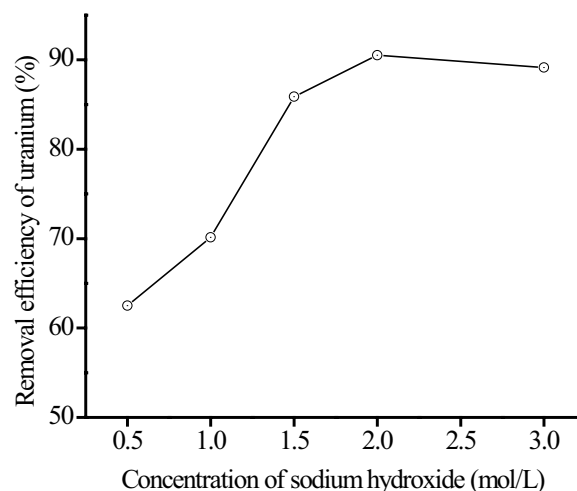

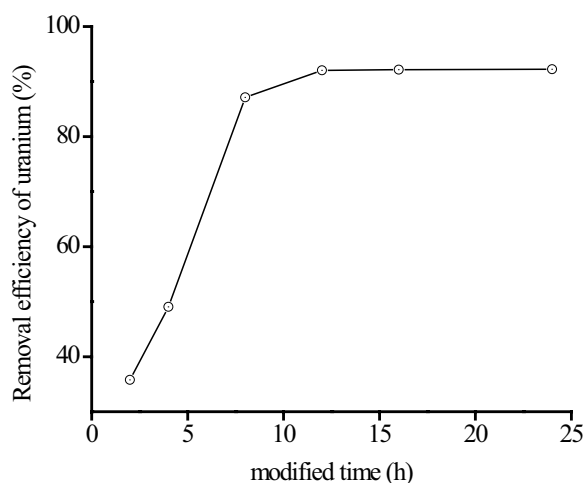Fig. 1. Effect of the concentration of sodium hydroxide on the removal of uranium.

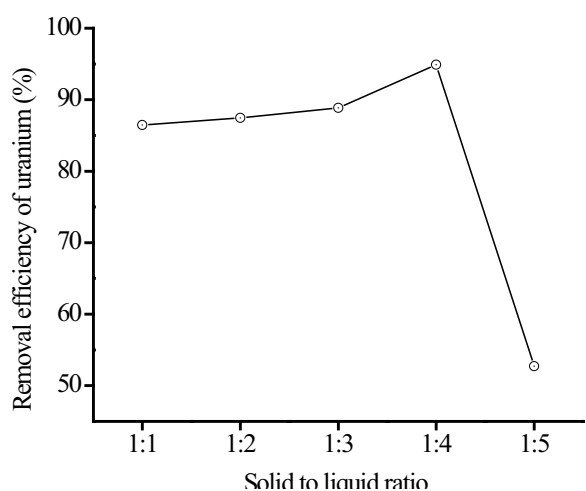Fig. 2. Effect of modified time on the removal of uranium.

Fig. 4. Effect of the particle size of a brick on the removal of uranium.

Fig. 3. Effect of solid to liquid ratio on the removal of uranium.

increased in comparing a 20 to a 140 mesh particle size of the brick powder. After that, the removal efficiency started to decrease. When the particle size was 140 mesh, the removal efficiency of uranium (VI) was 95.01%. Hence, the optimum particle size of brick powder was 140 mesh. In general, the smaller the particle size of the adsorbent, the larger the surface area, the more opportunities for metal ions to interact with the adsorption site, and the higher the metal adsorption rate. But when particle size reduced further, may occur due to particles between aggregation and precipitation, thus affecting the adsorption quantity of U (VI) [21].

3.5. Effect of adsorption time

Fig. 5 shows the effect of adsorption time on the removal efficiency of uranium (VI) by the modified brick powder. The removal efficiency rapidly increased within 3 h, which were 84.89% and 93.78%, respectively, when adsorption time was 1 and 3 h. The removal efficiency increased slowly when adsorption time further increase. Therefore, the present study suggests that optimal uranium removal may be achieved with adsorption time greater than 3 h.

The adsorption curve was consistent with the trend reported in most literatures [22–24]. The high initial adsorption rate may be because of existence of large number of empty sites onto adsorbent and interaction was developed between adsorbate and sorption sites [24,25]. When all the surface sites were occupied then the sorption slowed down due to movement of adsorbate deep into interior pores of adsorbent [24].

3.6. Effect of initial pH of the solution

The removal efficiency of uranium was strongly affected by the pH of the aqueous solution. The experimental results of the effect of the initial pH of the solution on the removal of uranium (VI) by modified brick powder are shown in Fig. 6. As shown in the figure, at pH 2, only 24.11% of U (VI) was removed by the adsorbent. Between pH 2 and 4, uranium removal increased quickly. The adsorption efficiency

the percentage gradually increased in solid to liquid ratio from 1:1 to 1:4, the removal efficiency was 94.90% at solid to liquid ratio 1:4, then the removal efficiency decreased rapidly with the increase of solid to liquid ratio. This is due to the increased dose of modifier (sodium hydroxide), so that the modification reaction is more sufficient, resulting in the increase of removal efficiency. However, the reasons for the rapid decrease in removal efficiency need further study, when the solid to liquid ratio exceeds 1:4. Solid to liquid ratio is an important parameter affecting the modification reaction [18–20]. For example, Xie et al. [19] found that with the increase of solid to liquid ratio, the interlayer spacing of montmorillonite increased gradually, but when the solid to liquid ratio increased to 8%, the interlayer spacing of montmorillonite decreased slightly.

3.4. Effect of particle size of the brick powder

As can be seen from Fig. 4, different particle sizes of the brick powder showed different removal efficiencies of uranium (VI). The removal efficiency of uranium (VI) gradually
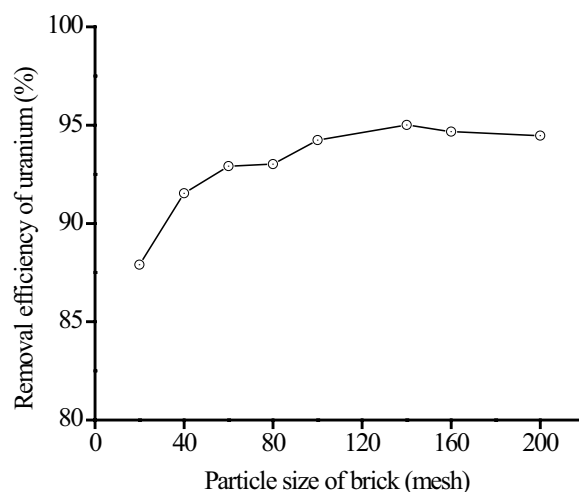
reached a peak of 96.17% at pH 6. Most of the wastewater containing uranium is a strongly acidic system; hence, the present study suggests that the optimum pH was 4.

One of the most critical parameters in the treatment of U (VI) by the adsorbent is the initial pH of the adsorption medium [5,26–28]. In the current work, we can find that the removal rate is lower when the range of pH is between 2 and 3, and it increases with the increase in the pH. When the solution pH is 2.0, there is a high concentration of H^+ and H_3O^+, which compete with other ions (uranyl) for the binding sites on the surface of the adsorbent [10,29], resulting in a low removal rate of U at this pH value. In addition, one or more kinds of U (VI) species could be involved in the adsorption [1,26], the distribution of U(VI) species is strongly dependent on pH values [26]. For example, the main U(VI) species in aqueous solution was predominated by positive UO_2^{2+} species at pH < 4.0, and then more hydrated U(VI) species such

as $UO_2(OH)^+$, $(UO_2)_4(OH)_7^+$, $(UO_2)_3(OH)_5^+$ were observed in the pH scope of 5.0–8.0 [3]. In the high pH value, U(VI) species change gradually from multinuclear hydroxide complexes to hydroxide complexes [26]. The adsorption of these species becomes easier because of the electronic attraction, thereby results in the high removal of U(VI) on the adsorbent. Hence, many literatures reported that the optimum pH is greater than or equal to 5 [2,4,27,28]. Compared with reported literature, the optimal pH of this study is lower and has better application prospects.

3.7. Effect of modified brick powder adsorbent dosage

The uranium (VI) removal by modified brick powder adsorbent is illustrated in Fig. 7. The dosage of adsorbent, between 0.2 and 1.2 g, did not significantly influenced the removal of uranium (VI). With increasing dose, uranium (VI) removal efficiency increased and then decreased. The optimum adsorbent dose was 0.4 g. At this dose, the removal efficiency of uranium (VI) was 96.04%. When the added dose was 0.6 g, the removal efficiency declined. Similar result was reported by researcher for cerium sorption onto tangerine peel [24]. Hence, the present study suggests that the optimum adsorbent dosage was 0.4 g.

3.8. Effect of initial uranium (VI) concentration

The initial metal ion concentration is particularly important and sorption of metal ions is dependent on it [24]. In the current work, the adsorption of uranium (VI) onto the modified brick powder was performed using solutions (pH 4) with different uranium (VI) concentrations ranging from 1 to 40 mg/L. As shown in Fig. 8, uranium (VI) removal efficiency increased with the rise of initial concentrations of the solutions, however, the removal efficiency decreased when the initial concentrations of uranium (VI) are more than 10 mg/L. This may be due to the saturation of the adsorption sites and increase in the number of ions competing for the available binding sites in the adsorbent for adsorption of uranium (VI) at higher concentration. In addition, we also found that the
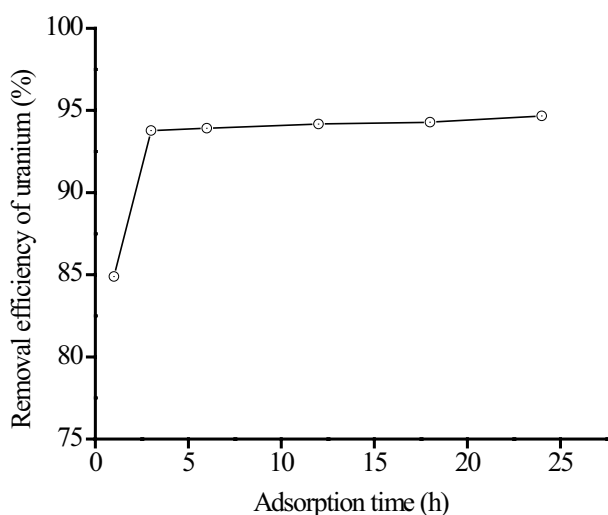

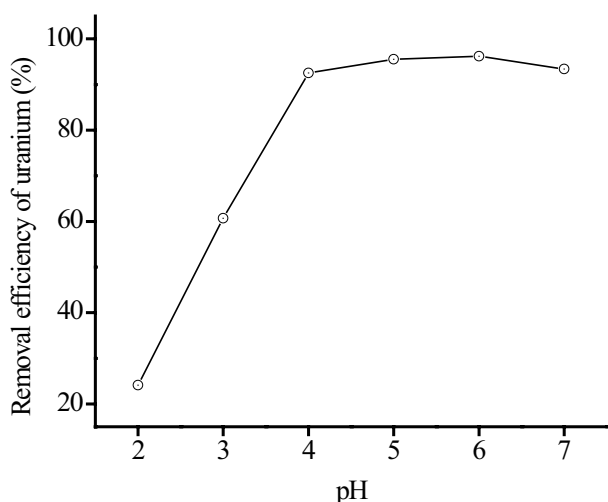Fig. 5. Effect of adsorption time on the removal of uranium.

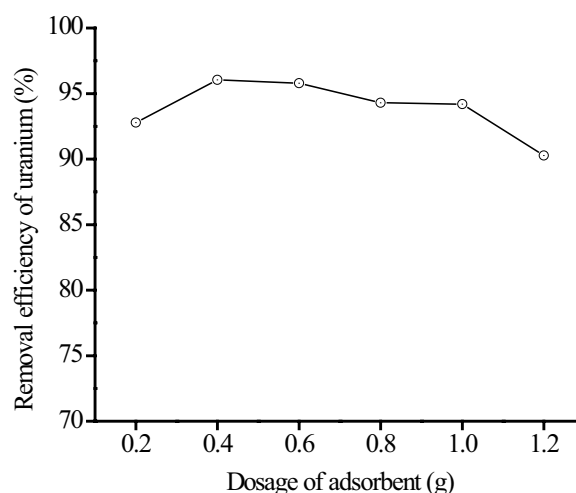Fig. 6. Effect of the pH of uranium solution on the removal of uranium.

Fig. 7. Effect of modified brick power adsorbent dosage on the removal of uranium.
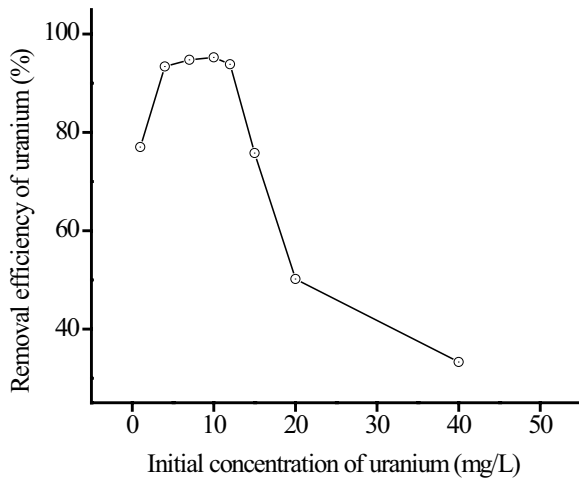
Fig. 8. Effect of the initial concentration of uranium on the removal of uranium.

removal efficiency can reach more than 93% at 4–12 mg/L of uranium concentration.

3.9. Desorption and reuse

From practical point of view, repeated availability was a crucial factor for an adsorbent [30,31]. To detect the reusability of the adsorbents, the adsorption and desorption cycles were repeated five times with 0.05 M HNO_3 as elution reagent. As shown in Fig. 9, during each adsorption–desorption cycle, the removal efficiency decreased by about 0.6%–2.6%. The final removal efficiency reached 89.66% at the forth cycles. The adsorption effect for metal ions changed slightly which might be related to the loss of active sites with the adsorption/desorption/regeneration processes [22,23].

4. Conclusions

In the current work, the clay brick powder was modified by sodium hydroxide and was prepared as an adsorbent
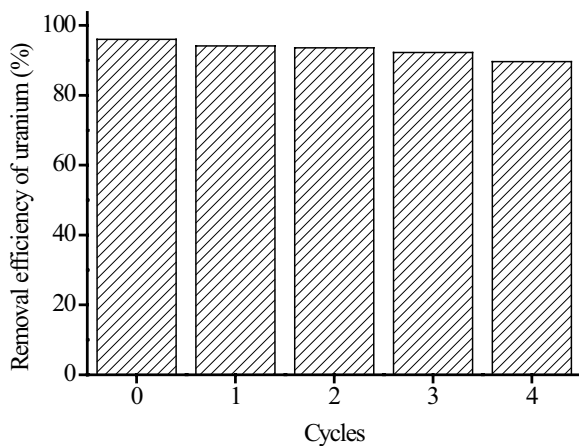

Fig. 9. Adsorption ratio of modified clay brick powder adsorbent on uranium.

to remove uranium (VI) from aqueous solution, and the sorption of U(VI) ions on modified clay brick powder adsorbent was investigated under different experimental conditions. The optimum modified conditions were 2 mol/L of sodium hydroxide, 12 h of modified time, 1:4 of solid to liquid ratio, 15 g of brick powder (140 mesh). The removal efficiency reached 95.28% at the initial concentration of 10 mg L^{-1}, pH 4, adsorption time of 180 min, and adsorbent dosage of 0.4 g. After four adsorption–desorption cycles, the removal efficiency of modified adsorbent still reached 89.66%.

Acknowledgements

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