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Cr (VI) removal from aqueous solutions by fly ash and fly ash composite filter material: Factorial experimental design

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The removal of Cr(VI) from aqueous solution by batch adsorption experiments using fly ash (FA) and composite filter material made of fly ash (FACFM) as adsorbents were investigated. The influence of pH, contact time on the selectivity and sensitivity of the removal process were investigated. The effect factors such as adsorbent dosage level, initial Cr(VI) concentration and temperature were studied through orthogonal experiment to investigate their degree of influence on the Cr(VI) adsorption process. Results show that FA and FACFM can be considered as efficient sorbents for the removal of Cr(VI) from aqueous solutions. It was also shown that increase in the adsorbent dosage level led to increase in Cr(VI) adsorption due to the increased number of adsorption sites, the adsorption process was highly pH dependent and the optimum pH was less than 3. Both adsorption rate and the removal ratio of FA were larger than that of FACFM because of its larger contact area and its powdery form, but concerning the intensity and ease of separation from aqueous solution, FACFM was more practical and can be used for wastewater treatment.

Key words: Cr (VI), fly ash (FA), fly ash composite filter material (FACFM), adsorption, orthogonal experiment.

INTRODUCTION

Disposal of effluents, containing heavy metals produced by processing industries, is a challenging task for environmental engineers due to their persistent and non-degradable nature. Chromium is of great concern due to the tendency of it been accumulated on vital organs of humans and animals, causing several health problems (Nriagu and Nieboer, 1988; Department of Health and Human Services, 2000). It is used in a variety of industrial applications; Sources of chromium waste leading to water pollution includes chrome plating, stainless steel fabrication, the manufacture of dyes and pigments, leather tanning, etc. (Nriagu and Nieboer, 1988;

Casarett and Doul, 1980).

Chromium exists usually in both trivalent and hexavalent forms in aqueous systems. The two-oxidation states of chromium have different chemical, biological and environmental characteristics (WHO, 1988). It is a bio-element in +3 oxidation state but mutagenic in +6 oxidation state. Cr(VI) has been reported to be a primary contaminant to humans, animals, plants and micro-organisms and it is known to be carcinogenic (Depart-ment of Health and Human Services, 1991; Cieslak, 1995; Raji and Anirudhan, 1998). The common concentrations of Cr(VI) found in typical wastewaters (such as electroplating or leather tanning wastewaters) are 50 to 100 mg/l (Xi et al., 1996). Due to environmental concern, discharge limits of both Cr(III) and Cr(VI) have been set up by most industrial countries. The tolerance limit of Cr(VI) for discharge into inland surface waters is 0.5 mg/l and 0.05 mg/l in potable water in China.

Various methods are used to remove chromium from aqueous solutions. The usual methods include chemical

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reduction (Chen et al., 2007), nanofiltration (Ahmed et al., 2006), bioaccumulation (Preetha and Viruthagiri, 2007), ion exchange (Cavaco et al., 2007), adsorption (Kumar et al., 2007; Arenas et al., 2007), etc. However, most of the technology processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal (Bai and Abraham, 2003).

Among which, adsorption is by far the most versatile and effective method for removing any contaminants like heavy metal, especially, if combined with appropriate regeneration steps. Activated carbon is the most widely used adsorbent in the industrial applications (Khalil and Girgis, 1998; Walker and Weatherley, 1997). However, the extensive use of activated carbon for metal removal from industrial effluents is expensive (Babel and Kurniawan, 2003), and limits its large application for wastewater treatment. Therefore, there is a growing interest in finding new alternative low-cost adsorbents for metal removal from aqueous solution, such as: microorganisms (Martins et al., 2006; Klen et al., 2007), wastes of food industries (Xuan et al., 2006; Ho and Ofomaja, 2006; Pavan et al., 2006; Jacques et al., 2007) and residuals of agricultural products (Brasil et al., 2006; Lima, et al., 2007).

Fly ash (FA) is a by-product during the combustion of coal in the electricity generation process. It is one of the main industrial solid wastes in China. According to statistics, the output of FA in China is about 1.6 billion tons in 2000, and it may reach 2.0 billion tons in 2010 (Cao et al., 1998).

The stacking of FA will occupy much land, and will pollute soil, groundwater and air. Many studies have shown that FA has large specific surface and the amount of active components such as silicon and aluminum (Liu et al., 2001; Jiao et al., 2007), which accounts for its good adsorption capacity and thus can be used as an adsorbent for removal of heavy metal from aqueous solution.

Some experimental research results showed that FA had a good effect in adsorbing Cr (VI) from aqueous solution (Liu and Yang, 2008; He et al., 2009).

Most FA is in powdery form and with weak intensity, and it is inconvenient to apply directly into wastewater treatment. In order to make the maximum use of the adsorption capacity of FA, fly ash composite filter material (FACFM) was made.

In comparison with FA, FACFM has high-strength and can be used in wastewater treatment directly.In this study, FA and FACFM were used as adsorbents to remove Cr(VI) from aqueous solutions and the adsorption properties were compared.

The effects of pH, contact time on the adsorption processes were investigated. Adsorbent dosage level,

Initial metal ion concentration and temperature were considered as the factors used to study their effect on the degree of the adsorption process through orthogonal experiment.

MATERIALS AND METHODS

Adsorbents and its sources

The samples of FA and FACFM were obtained from Cikon Co. (Jiangsu, China). FA was from a coal thermal power plant, which was dark grey in color and powdery in appearance. FACFM is spherical in shape with diameter of 3 to 6 mm and light yellow in color. The constituents of FACFM include fly ash (which occupied more than 50% weight of FACFM), attapulgite, kaolin and agglomerant. FACFM was found in the hard epidermis and there were much micro porosity in its surface and inner. All the adsorbents were washed by deionised water, filtered, dried in a drying oven at $105 \pm 5°C$ for 24 h and then cooled to room temperature in a desiccator for use in adsorption studies.

Reagents

All the primary chemicals used to prepare reagent solutions were of analytical reagent grade supplied by Nanjing Chemical Industries Ltd. (China). A stock solution containing 1000 mg/L of Cr(VI) was prepared by dissolving 1.4145 g quantity of AR grade $K_2Cr_2O_7$ in 500 ml deionized water and was used to prepare the sorbate solutions of different concentrations by appropriate dilution for different experiments performed.

Other chemicals included: diphenylcarbazide, acetone, sulphuric acid, phosphoric acid, and sodium hydroxide.

Equipments

Diphenylcarbazide spectrophotometric method was used to determine the concentration of Cr(VI). A mercury porosimeter (Autopore 9500, Micromeritics, USA) was used to determine the porosity of FA. A digital pH meter of PSI CO. LTD, Shanghai, China (PHS-3C) was used for pH measurement.

Other instruments included: UV-Vis Spectrophotometer (SP-752), Shanghai Spectrum Instruments Co., Ltd; electric tachometer indicator thermostatic drying oven (GZX-9140MBE); oven oscillator (ZD-85); electronic analytical balance (JA2003); super pure water machine (KL-RO-20); scanning electron microscope (Quanta, FEI) and gas bath constant temperature oscillator (CHA-SA).

Batch adsorption experiments

A typical sorption experiment was conducted by taking proper sorbents in 100 ml solution sample with 20 mg/l Cr(VI) concentration in a 250 ml stopper conical flask, kept them on an oscillator at 180 rpm and fit temperature for the desired contact time. The necessary adsorbent batch experiments were carried out at designed temperature, contact time, pH value and adsorbent dosage level. The pH value of the solution was adjusted by adding negligible volumes of 0.1 M NaOH or HCl. The contents of the flask were filtered through filter and then the filtrate was analyzed for remaining Cr(VI) concentration in the samples.

Table 1. Factorial experimental design of orthogonal experiment.

Influence factor	Factor 1: initial Cr(VI) concentration: C_0 (mg/L)	Factor 2: Adsorbent dosage level: m (g/L)	Factor 3: temperature: T(°C)
Levels	1, 2, 3, 4	1, 2, 3, 4	1, 2
Correspondence values	5, 10, 20, 30	10, 20, 40, 60	25, 50
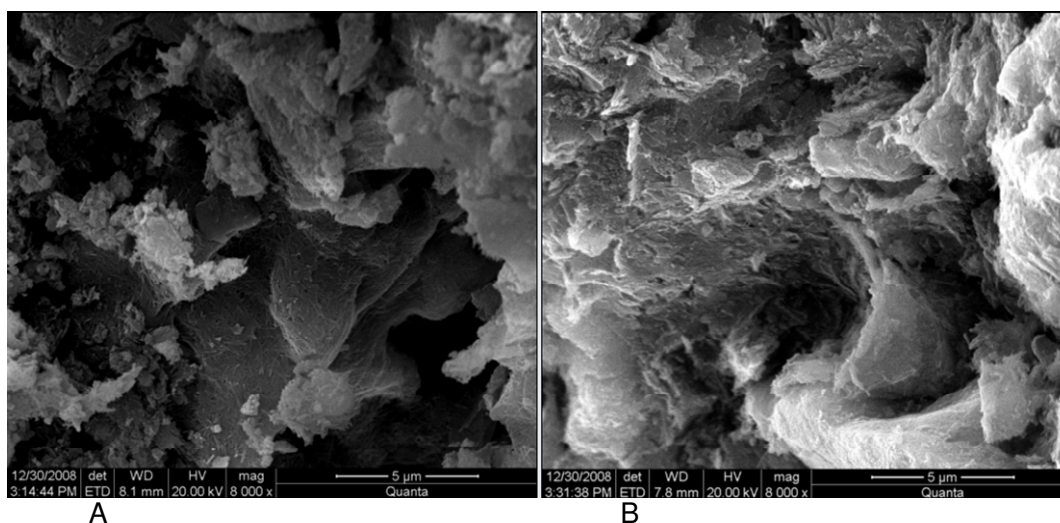
Figure 1. Micropore size distribution of FACFM. (A) The SEM images of the surface of the FACFM (8000×); (B): The SEM images of the inner of the FACFM (8000×).

$$Removal \quad ratio \quad = \frac{C_0 - C_e}{C_0} \times 100 \ \%$$

Where, C_0 (mg/l) is the initial Cr(VI) concentration and C_e (mg/l) is the equilibrium concentration of Cr(VI).

To determine the variation of Cr(VI) adsorbed by FA and FACFM with contact time, batch adsorption studies were carried out by using initial Cr (VI) concentration of 20 mg/l and dosage of adsorbent 30 g/l. Time was changed from 0 to 120 min, and Cr(VI) concentration was determined at regular time intervals of 10 min at pH 3.0 with temperature of 25 ± 2°C

The variation in the adsorption of Cr (VI) onto FA and FACFM as a function of pH was conducted over pH range of 1.4 to 10.1 using 100 ml of 20 mg/l Cr(VI) solution with adsorbent concentration 30 g/l for 90 min at 25 ± 2°C.

There are many factors that affect the adsorption properties of Cr(VI) in the solution. In order to find out the relation of primary and secondary influencing factors, orthogonal experiment method was used. According to some authors (Xuan et al., 2006; Ho and Ofomaja, 2006; Pavan et al., 2006; Jacques et al., 2007), adsorbent dosage level, temperature and initial Cr(VI) concentration were the main influencing factors. In this study, the influence of the earlier mentioned three factors was studied by taking different concentration of Cr(VI) solution at pH 3 for contact of 90 min with adsorbent dosage level varying from 10 to 60 g/l and initial Cr(VI) concentration varying from 5 to 30 mg/l at different temperatures by orthogonal experiments. The designed experimental parameters are shown in Table 1.

According to the earlier mentioned influencing factors and level values, $L_{16}(4^4 \times 2^3)$ orthogonal table was used to arrange the experiments.

RESULTS AND DISCUSSION

Characterization of the adsorbent materials

Characterization of FACFM

Figure 1 shows the stereoscan photograph of the surface and the inner of the FACFM by scanning electron microscope. The surface of the material observed was rough, uneven and with much gaps, and some of the sizes of the porous particle were about 5 μm, and most of the sizes of the porous particle were not more than 5 μm. The inner of the material was porous and rough, and the size of the porous particle was less than 5 μm.

Characterization of FA

After dried and cooled, all FA used in the experiment were sieved. The size of the FA selected for use ranged from 0.25 to 0.074 mm. Mercury porosimeter test showed that the total intrusion volume of the FA is 0.686 ml/g,
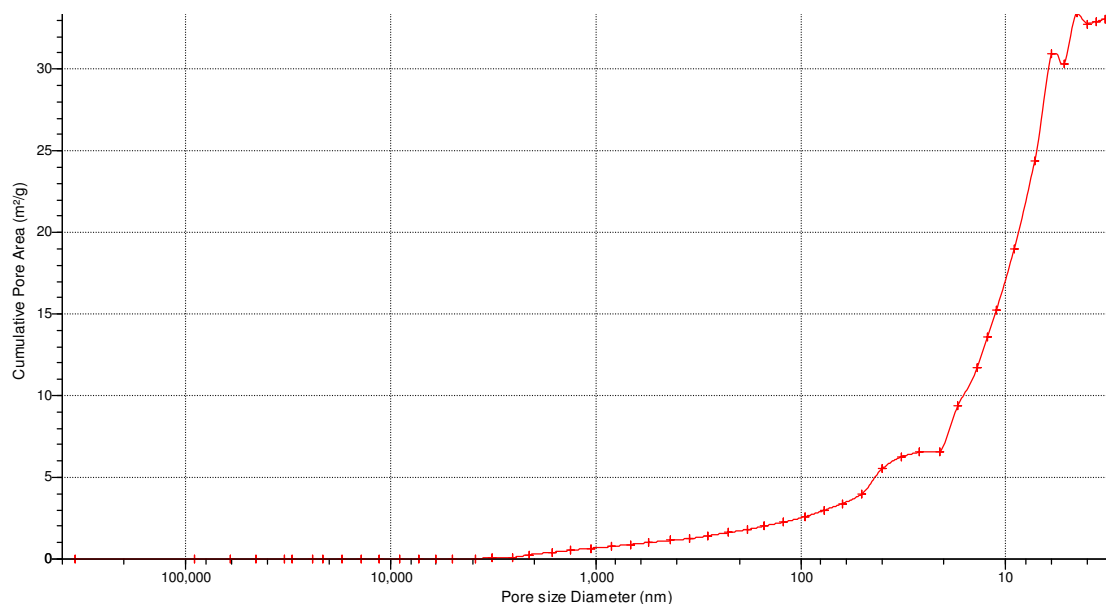
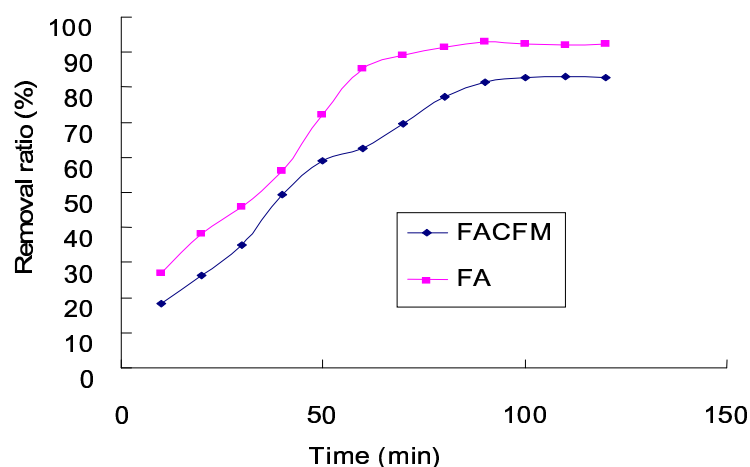**Figure 2.** Cumulative pore area vs. pore size of FA.

Figure 3. Effect of contact time on the adsorption of Cr(VI) by FA and FACFM. pH = 3, initial Cr(VI) concentration = 20 mg/L, adsorbent dosage = 30 g/L, temperature = 25 ± 2°C.

total pore area is 33.015 m^2/g, average pore diameter (4V/A) is 83.1 nm, median pore diameter (area) is 10.3 nm, apparent (skeletal) density is 2.5993 g/ml and porosity is 64.5%. According to the results obtained from porosimeter analysis, the least diameter of the pore is about 3.02 nm. 45.5% of the size of the pore is less than 1000 nm. Analysis of the results according to the test is presented in Figure 2. Results show that FA is rich in porous particle and with large specific surface area.

Effect of time

Experiments were conducted by using initial Cr(VI)

concentration (20 mg/l), and the dosage of adsorbent was 30 (g/l), and time changed from 0 to 120 min. The Cr(VI) concentration of the solution was determined at regular intervals of 10 min with temperature at 25 ± 2°C. Many research papers showed that the maximum adsorption of Cr(VI) occurred at pH = 2 to 3 (Chen and Chen, 2008) by different adsorbents; so in this study, pH was adjusted to 3. Results of this study are shown in Figure 3.

As for FA, it is evident from Figure 3 that the removal ratio of Cr(VI) increased sharply within 60 min, then the increase rate descended, and no appreciable change in terms of adsorbing capacity was observed. The residual
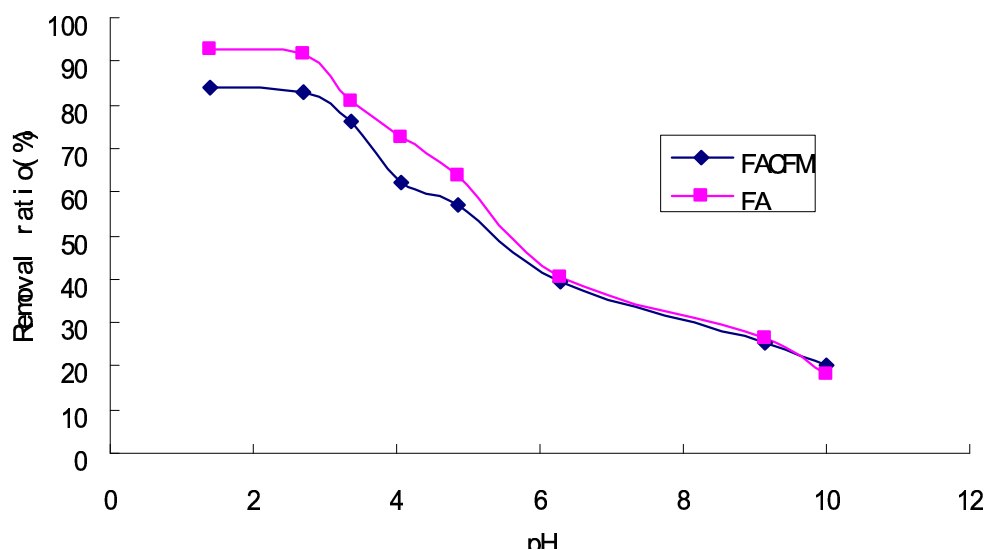
Figure 4. Effect of pH on the adsorption of Cr(VI). Temperature = 25 ± 2°C, contact time = 100 min, adsorbent dosage = 30 g/L, initial Cr(VI) concentration = 20 mg/L.

Table 2. Composition of Cr(VI) solution as a function of pH.

pH value	Predominant species
<1	H_2CrO_4
2-4	$Cr_2O_7^{2-}$
2-6	$HCrO_4^-$, $Cr_2O_7^{2-}$
6-8	$Cr_2O_7^{2-}$, CrO_4^{2-}
>8	CrO_4^{2-}

Cr (VI) concentration changed minimally after 90 min. At 60 min, the removal ratio was 85.35%, while at 90 min the removal ratio was 92.31%. As for FACFM, the removal ratio increased sharply within 90 min and no appreciable change in terms of adsorbing capacity was seen. The residual ion concentration was almost unchanged after 90 min. At 90 min, the removal ratio was 81.32% while at 120 min, the removal ratio was 82.76%.

The reason being that in the initial stage, there were many adsorbent sites in the adsorbents, and with time, those sites were occupied by Cr(VI). Also, the concentration difference between solid and liquid phase became smaller with time, so the adsorption rate and the desorption rate reached equilibrium, which leads to low growth of removal ratio. It is also evident from Figure 3 that the adsorption rate of FA was faster than that of FACFM, and the final removal ratio of FA was also higher than that of FACFM, for the reason, FA was in the powder state, and the contact area of FA with Cr(VI) was larger than that of FACFM.

It was thus considered that the process reached its saturation stage within 100 min for both adsorbents. Consequently, the rest of the batch experiments of

adsorption were conducted using 100 min as contact time to make sure that equilibrium was reached.

Effect of pH

Adsorption experiments for the effect of pH were conducted over pH range of 1.4 to 10.1 using 100 ml of 20 mg/l Cr(VI) concentration solution with adsorbent concentration of 30 g/l for 100 min at 25 ± 2°C. Results of the study are shown in Figure 4.
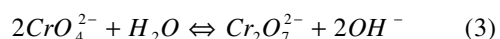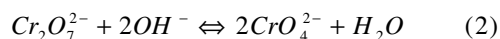
Results show that high efficiency in Cr(VI) removal was observed only under acidic conditions for both FA and FACFM (pH = 1.4 to 2.7). The best pH value for Cr(VI) removal using FA and FACFM was found to be less than 3, and in this range of pH value, the removal ratio of both adsorbents was greater than 80%. At higher pH value, a decrease in adsorption of Cr(VI) was obtained which may be due to the ionic repulsion between anionic sites of adsorbent surface and chromate ions.

The removal of Cr (VI) by both adsorbents was dependent upon pH of the solution which affects degree of ionization and speciation of adsorbate species. Cr(VI) forms stable complexes such as $Cr_2O_7^{2-}$, $HCr_2O_7^{2-}$, CrO^- and $HCrO^-$. The chemistry of Cr(VI) is greatly dependent on pH of the solution (Ansari and Khoshbakht, 2007). At pH value below 1, the predominant species is H_2CrO_4, Cr(VI) usually exists in the anionic form, as $Cr_2O_7^{2-}$, $HCrO_4^-$ or $Cr_2O_7^{2-}$ forms depending on pH and concentration (Equations 1 to 3 and Table 2). In acidic media (pH 2 to 4), Cr(VI) exists mostly in the form of dichromate ($Cr_2O_7^{2-}$) ions. At pH between 2 and 6, $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions exist in equilibrium and under alkaline conditions (pH > 8), it exists predominantly as chromate

Table 3. Adsorption performance experiments of FACFM.

Experiment number	Effect factor			Removal ratio (%)
	Initial Cr(VI) concentration: C_0 (mg/L)	Adsorbent dosage level: m (g/L)	Temperature: T (℃)	
1	5.00	10.00	25.00	27.33
2	5.00	20.00	25.00	29.74
3	5.00	40.00	50.00	31.89
4	5.00	60.00	50.00	35.11
5	10.00	10.00	50.00	25.95
6	10.00	20.00	50.00	27.15
7	10.00	40.00	25.00	34.81
8	10.00	60.00	25.00	36.42
9	20.00	10.00	25.00	25.19
10	20.00	20.00	25.00	26.33
11	20.00	40.00	50.00	28.81
12	20.00	60.00	50.00	31.16
13	30.00	10.00	50.00	26.50
14	30.00	20.00	50.00	28.20
15	30.00	40.00	25.00	32.05
16	30.00	60.00	25.00	33.30
K1	124.08	104.96	245.16	
K2	124.32	111.43	234.78	Σ=479.95
K3	111.49	127.56		
K4	120.05	135.99		

anion.

$$Cr_2O_7^{2-} + H_2O \Leftrightarrow 2HCrO_4^{-} \qquad (1)$$
$$Cr_2O_7^{2-} + 2OH^{-} \Leftrightarrow 2CrO_4^{2-} + H_2O \qquad (2)$$
$$2CrO_4^{2-} + H_2O \Leftrightarrow Cr_2O_7^{2-} + 2OH^{-} \qquad (3)$$

The results also showed that the removal ratio of FA was better than that of FACFM. Cr(VI) removal was negligible under alkaline conditions.

However, the exact mechanism for Cr(VI) sorption is not very clear. Taking into consideration the short time used to reach the equilibrium time and the high dependency on pH, Cr(VI) removal by FA and FACFM seems to be occurring mostly via anion exchange process.

Effect of initial Cr(VI) concentration, adsorbent dosage level and temperature by orthogonal experiment

Results of adsorption performance experiments of FACFM

Each experiment was conducted by using different initial Cr(VI) concentration and adsorbent dosage level, and contacting time of 100 min with pH adjusted to 3. The remaining Cr(VI) concentration of the solution was determined and removal ratio was calculated. The results of the orthogonal experiment using FACFM as adsorbent are shown in Table 3.

The analysis of the data is shown in Table 4. Results show that the value of $F>F_{0.01}$ of factors 1 and 2 gave reasons for the initial Cr(VI) concentration and adsorbent dosage level which particularly had a marked influence on the removal of Cr(VI). With the increase of initial Cr(VI) concentration, the removal ratio of Cr(VI) decreased, while with the increase of adsorbent dosage level, the removal ratio of Cr (VI) increased. In the case of factor 3, the value of $F_{0.05}<F<F_{0.01}$, which showed that temperature had marked influence on the removal of Cr(VI), and with the increase of temperature, the removal ratio of Cr(VI) increased. In the case of practice, FACFM was more suitable for treating low Cr (VI) concentration wastewater as compared to the higher concentration. Multi-reactors series can be used to get good treatment effect.

Results of adsorption performance experiments of FA

Experiment was conducted by using different initial Cr(VI)

Table 4. Checklists about analysis of variance in the orthogonal tests of FACFM.

Source of variation	Sum of deviation square	Degree of freedom	Mean square	F	$F_{0.05}$	$F_{0.01}$
Factor 1(c_0)	26.94	3	8.98	8.06	4.07	7.59
Factor 2(m)	153.11	3	51.04	45.83	4.07	7.59
Factor 3(T)	6.73	1	6.73	6.05	5.32	11.26
Error	8.91	8	1.11			

Table 5. Adsorption performance experiments of FA.

Experiment number	Effect factor			Removal ratio (%)
	Initial Cr(VI) concentration: C_0 (mg/l)	Adsorbent dosage level: m (g/l)	Temperature: T(℃)	
1	5.00	10.00	25.00	22.23
2	5.00	20.00	25.00	26.52
3	5.00	40.00	50.00	26.79
4	5.00	60.00	50.00	31.62
5	10.00	10.00	50.00	21.92
6	10.00	20.00	50.00	23.26
7	10.00	40.00	25.00	31.05
8	10.00	60.00	25.00	31.99
9	20.00	10.00	25.00	23.58
10	20.00	20.00	25.00	23.98
11	20.00	40.00	50.00	26.66
12	20.00	60.00	50.00	31.16
13	30.00	10.00	50.00	26.50
14	30.00	20.00	50.00	27.40
15	30.00	40.00	25.00	29.99
16	30.00	60.00	25.00	34.47
K1	107.17	94.23	223.80	
K2	108.21	101.16	215.32	
K3	105.38	114.49		Σ=439.12
K4	118.35	129.24		

concentration and adsorbent dosage level, contact time of 100 min with pH adjusted to 3. The remaining Cr(VI) concentration of the solution was determined and removal ratio was calculated. The results of the ortho-gonal experiment using FA as adsorbent are shown in Table 5.

The analysis of the data is shown in Table 6. Results show that the value of $F_{0.05}<F<F_{0.01}$ of factor 1 explain that initial Cr(VI) concentration had marked influence on the removal of Cr(VI). The value of $F>F_{0.01}$ of factor 2 explain that adsorbent dosage level had particularly marked influence on the removal of Cr(VI). The value of $F<F_{0.05}$ of factor 3 explain that temperature had no marked influence on the removal of Cr(VI).

When comparing the adsorption performance of FA and FACFM, the F values of the three factors for FA were all smaller than that of FACFM, which illustrated that the three factors had less influence on the adsorption characteristics of FA than their influence on FACFM. That is to say, it is not easy to improve the removal ratio of Cr (VI) by adsorption using FA by changing the experimental factors.

In the case of engineering application, though FA had higher removal ratio to Cr(VI) than FACFM because of its higher specific surface area, it was difficult for it to be separated from the wastewater because of its powder

Table 6. Checklists about analysis of variance in the orthogonal tests of FA.

Sources of variation	Sum of deviation square	Degree of freedom	Mean square	F	$F_{0.05}$	$F_{0.01}$
Factor 1(c_0)	25.53	3	8.51	4.16	4.07	7.59
Factor 2(m)	179.26	3	59.75	29.22	4.07	7.59
Factor 3(T)	4.49	1	4.49	2.20	5.32	11.26
Error	16.36	8	2.04			

state; as such, FACFM had more intensity and was easy to separate from water, so it has more practical value than FA.

Conclusion

In this study, batch adsorption studies for the removal of Cr(VI) from aqueous solutions was carried out by using FA and FACFM as adsorbents. It was found that FA and FACFM can be considered as efficient sorbents for the removal of Cr(VI) from aqueous solutions. The obtained results may be summarized as follows:

(1) Increase in adsorbent dosage led to increase in Cr(VI) adsorption due to increased number of adsorption sites.
(2) The pH variation studies showed that the adsorption process was highly pH dependent. The optimum pH range for the removal was less than 3. Adsorption equilibrium was attained within 100 min. Cr(VI) removal by FA and FACFM seems to be occurring mostly via anion exchange process.
(3) Both the adsorption rate and the removal ratio of Cr(VI) by FA were larger than that of FACFM because of its larger contact area and powder state, but with regards to the intensity and difficulty for it to be separated from the aqueous, FACFM was more practical and can be used for wastewater treatment.

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