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THE REMOVAL OF Cr(VI) FROM THE AQUEOUS SOLUTION BY GRANULAR FERRIC HYDROXIDE (GFH)

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COMMUNICATION

Keywords: Granular ferric hydroxide (GFH), adsorption isotherms, batch tests, column tests, chromium.

Abstract: In this work, sorption of chromium on granular ferric hydroxide (GFH) has been investigated using batch and column techniques. The adsorption behavior of Cr on GFH, depending on pH, contact time and sorbent amount were studied. The equilibrium adsorption capacity of GFH for Cr was measured and extrapolated using Freundlich isotherms. Metal ions bounded to the GFH could be recovered by alkaline solution, and the GFH can be recycled. The sorption capacity of GFH was 25.0 mg/g. The ion exchange of chromium on GFH follows pseudo-first-order kinetics. The intraparticle diffusion of chromium on GFH presents the limiting rate. The results indicated practical value of this method for industry and also provide strong evidence to support the proposed thesis about the adsorption mechanism.

INTRODUCTION

Chromium(VI) is released into the environment through a large number of industrial operations, including metal finishing industry, leather, tanning, textile and pulp processing factories [9].

Removal of Cr(VI) from wastewater is essential due to their toxicity. Two possible oxidation states for chromium are: Cr(III) and Cr(VI). Cr(VI) is a strong oxidant and potential carcinogen. It has toxic influence on plants, animals, humans and microorganisms and is associated with the development of various chronic health disorders, including organ damage, dermatitis and respiratory impairment [10].

Many previous works have attempted to find reasonable methods to remove heavy metals from wastewater, such as: electrochemical [6], chemical precipitation [1], adsorption [7]

As one of the most promising techniques for removal of chromium from industrial wastewater, adsorption technology has been employed for many years and effectiveness of various adsorbents has been demonstrated [8]. Jing Hu using maghemite nanoparticles to remove Cr(VI) reached the maximum adsorption at pH 2.5 [5]. A number of investigators have studied the removal of inorganic metal ions in particular chromium from aqueous solution using different adsorbents. Adsorption not only removes heavy metals from liquid phase but also allows regenerating and recycling them back into the industrial process.

A previous study [1–3] has shown that GFH is a promising material for the removal of arsenic and phosphorus from the natural water by adsorption. Badruzzaman showed that arsenate adsorption isotherm data were fitted with the Freundlich model [1]. Resulting K_F values were 3.60 and 4.55 μg As/mg dry GFH. At pH 7.0 Driehaus [2] obtained an adsorption density 17 mg As/g dry GFH at an equilibrium liquid phase concentration of 10 μg/dm^3. The difference in adsorption capacity between Badruzzaman and Driehaus could be due to differences in initial concentration of As(V) or background water composition [1, 2]. Driehaus does not mention a pH buffer, but bicarbonate was used in his study [2].

Genz [3] investigated the advanced phosphorus removal by adsorption on activated aluminum oxide (AA) and GFH in water treatment, GFH showed a higher maximum capacity for phosphate and a higher affinity at low P concentrations compared to AA. The achieved loadings from 0.1 and 0.3 mg/dm^3 equilibrium of phosphorus concentrations at pH 8.2 amount to 7.9 and 12.3 mg/g for GFH and to 4.6 and 7.9 mg/g for activated aluminum. For reloading of phosphorus the regeneration of GFH by 0.6 M NaOH seems most effective by the volume ratio of NaOH to the bed volume 100:1. Since, typically between two and four bed volumes of regenerate are used in adsorption filters a much higher consumption of NaOH is used. It was also found that the adsorption process was influenced by the matrix pH, the contact time and the capacity of the GFH material.

In this study, GFH as a sorbent was investigated for the removal of Cr(VI) from wastewater, recovery of GFH, and presentation of Cr(VI) adsorption mechanism onto GFH. Another goal was to obtain significant data for the application of this technique on industrial scale and make comparisons of low-cost adsorbents for treating wastewaters with chromium(VI).

MATERIAL AND METHODS

Adsorbent media

GFH was obtained from Wasserchemie GmbH & Co. KG, Germany, applied in batch and fixed-bed column tests. The characteristic of GFH:

- water contents 36.5–42%,
- grain size 0.32–2 mm,
- grain density 1.5 kg/dm^3,
- $Fe(OH)_2$ contents 52–57%,
- flow rate 5–20 m/h,
- pH range 3,5–9,0,
- concentration of Fe in water < 0,2 mg/dm^3.

The results are presented on a dry GFH mass.

Instrumentation

A Unicam 919 atomic adsorption spectrometer (AAS Unicam, England) was used for chromium(VI) analysis. The primary wavelength was 357.9 nm. The gas used in burner was acetylene. Sensitivity of the method was 0.05 mg/dm^3. The possible negative effect of other metals presence was overcome by addition of a buffer. A pH meter CI-316 (ELMETRON, Poland) was used for pH measurement. Peristaltic pump (pp1B-05A ZALiMP, Poland) for column tests.

Chemicals

pH adjustment was done by 0.1 M NaOH or HCl.

Distilled water was used throughout the work. Stock solutions of 1000 mg/dm^3 chromium(VI) was prepared by dissolving 2.8292 g of potassium dichromate ($K_2Cr_2O_7$) in distilled water. No other salts were added to adjust the ionic strength.

The pH-meter was calibrated using standard buffer solutions of known pH.

Batch experiments

Working solutions with chromium(VI) concentration of 5 mg/dm^3 were prepared from the standard solution of potassium dichromate diluted to 250 cm^3 with distilled water. To develop adsorption isotherms, the method of adding different quantities of adsorbent (0.1 g, 0.15 g, 0.2 g, 0.25 g, 0.3 g, 0.35 g, 0.4 g, 0.45 g, 0.5 g dry matter) to a constant solution volume at the same initial concentration of chromium was used. Experiments were repeated with different pH value (3.5, 4.0, 5.0, 6.95). pH value was corrected by 0.1 M HCl.

After adjusting pH and adding GFH, the contents of flasks were stirred for 7 h. This equilibration time was determined in a corresponding kinetic experiment. After stirring the sample was filtered, and only then the final concentration of chromium was measured.

Fixed bed column experiments

A glass column with a diameter 1.4 cm was filled with GFH on glass wool support to the high of 16.7 cm. Column was supplied with chromium wastewater for a period of 4 days continuously as fixed-bed down-flow reactors. Before starting to exploit the column, the solubility of filtering material was checked and in the range of pH accepted by Manufacturer very low solubility was observed (max. conc. of Fe < 0.03 mg/dm^3). Chromium contained wastewater was pumped through the GFH column with a peristaltic pump, at the rate of 10 m/h. (This flow rate is the average between minimum and maximum given by Manufacturer). The contact time was 1 minute. The homogeneous surface diffusion model was used to describe the column batch data [5].

Regeneration studies

The loaded column was regenerated after the first loading with 0.6 M NaOH solution with the 100 cm^3 portions of reagent. For reconditioning the column was rinsed with distilled water and pH was readjusted before reloading.

FUNDAMENTAL PRINCIPLE

The metal concentration on the sorbent increases until equilibrium is reached between the solid and liquid phases in the system. The concentration of metal on the medium is calculated as the difference between the original concentration of the solution and the measured concentration in the liquid phase after contact. The mass balance may be expressed as:

$$m\,(N_e - N_o) = V\,(C_o - C_e) \tag{1}$$

where N = 0, let $x = V\,(C_o - C_e)$ so

$$N_e = x/m \tag{2}$$

The N_e value means the mass ratio of metal to sorbent. The most frequently used isotherm for the mathematical representation of this type of data is the Freundlich equation (3):

$$N_e = K_F C_e^{1/n} \tag{3}$$

Equation (3) can be linearized as logarithm:

$$\log N_e = \log K_F + (1/n) \log C_e \tag{4}$$

where:
V – volume of solution [dm^3],
x – mass of metal captured by media [mg],
C_o – initial liquid phase metal concentration [mg/dm^3],
C_e – equilibrium liquid phase metal concentration [mg/dm^3],
N_e – equilibrium metal concentration on media [mg/g],
m – mass of the media [g],
K_F – Freundlich isotherm constant [l/g].

RESULTS AND DISCUSSION

Equilibrium adsorption isotherms

The results obtained during the batch scale experiments are shown in Figure 1 for GFH at pH = 3.5, 4.0, 5, 6.95. Initial concentration of Cr(VI) C_o was 5 mg/dm^3. The pH-value was lowered using 0.1 M HCl.

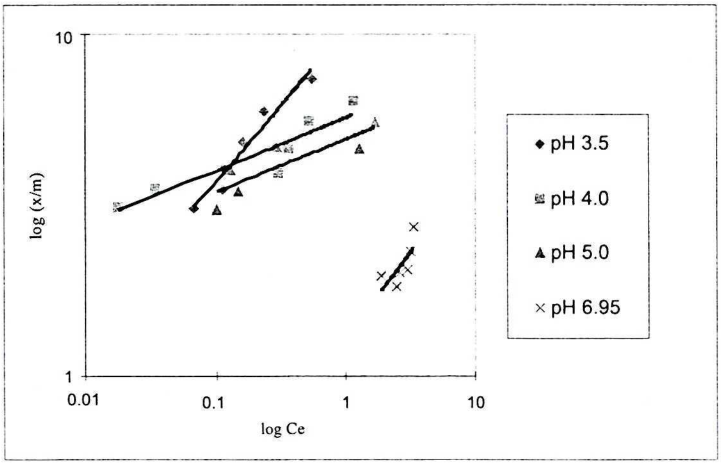

Fig. 1. Correlation between final concentration of Cr(VI) and x/m ratio on GFH at various pH

Effect of pH on adsorption

The effect of pH on the removal of chromium by its adsorption on GFH (0.15 g), is shown in Figure 2. It can be seen that pH of the solution plays a very important role in the adsorption of chromium. At pH = 6.95, GFH adsorption capacity was 2.59 mg/g, and at pH = 3.5 the capacity increased to 7.46 mg/g. A decrease in pH from 6.95 to 3.5 led to higher loading for adsorbents due to the more positively charged adsorbent surface at acidic pH.

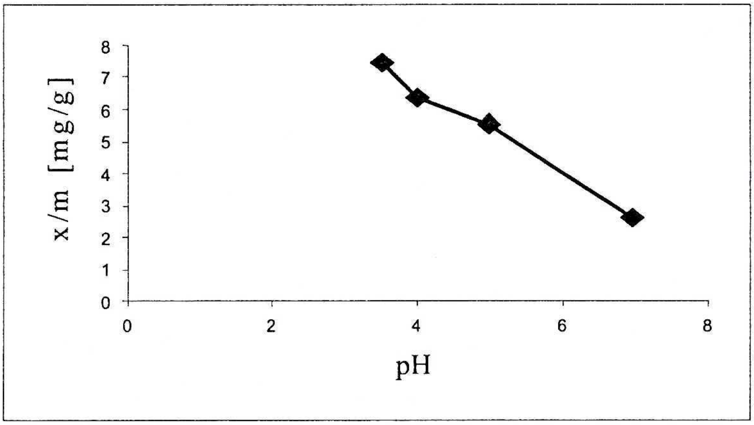

Fig. 2. Effect of pH on sorption capacity of GFH

Effect of GFH dosage on adsorption

Figure 3 shows the degree of removal of chromium from the solution at different doses of GFH and with different pH values. The GFH doses varied from 0.15 to 0.4 g. The experiment shows that for the maximum removal of 5 mg/dm^3 of chromium from 250 cm^3 sample requires a minimum GFH dosage of 0.4 g. The experimental results reveal that the chromium removal efficiency increases up to an optimum dosage beyond which the removal efficiency does not change. It is clear that the equilibrium concentration decreases with increasing adsorbent doses for a given initial chromium concentration, because by constant initial metal concentration, increasing adsorbent doses provides a greater surface area or adsorption sites [5].

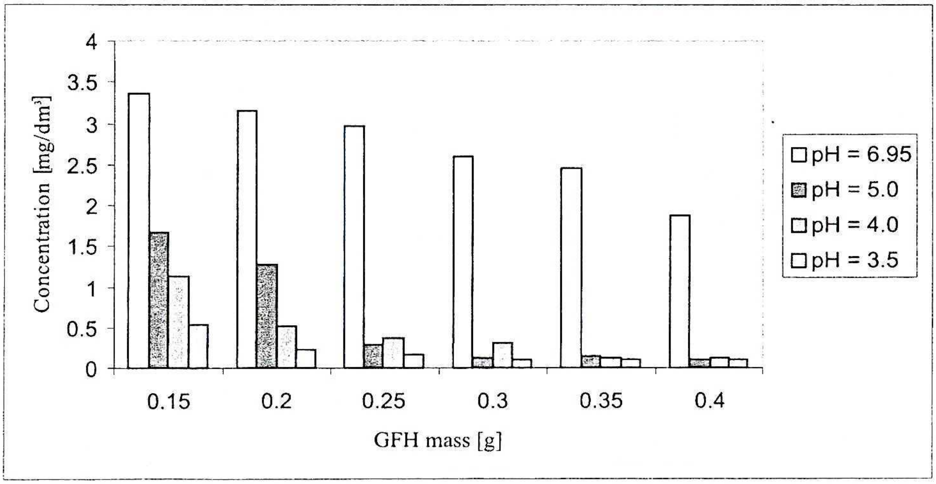

Fig. 3. Cr(VI) removal depending on GFH masses

Chromium removal behaviors

The chromium removal kinetic was established using in each case 36.30 g GFH. Experiments were repeated at different pH value in order to find out the equilibrium time. The reaction mixture consisted of 1 dm^3 of wastewater with initial concentration of 1400 mg Cr(VI)/dm^3 (this concentration was calculated proportional to the amount of GFH used in previous experiment). At fixed time interval a sample was withdrawn and analyzed. The result is shown in Figure 4 at pH = 5.68 and 3.5. The highest efficiency of chromium removal took place in 360 min, after which approximately 65% Cr was removed.

From the reported data it can be seen that the initial adsorption kinetics is very high (the trend is almost vertical) for all values of pH and that it rapidly decreases with time. Since the initial kinetics is mainly related to the external mass transfer resistance, the external diffusion is very rapid. Furthermore, we observed that adsorption capability becomes very low after 360 min, which means that GFH adsorption is close to saturation.

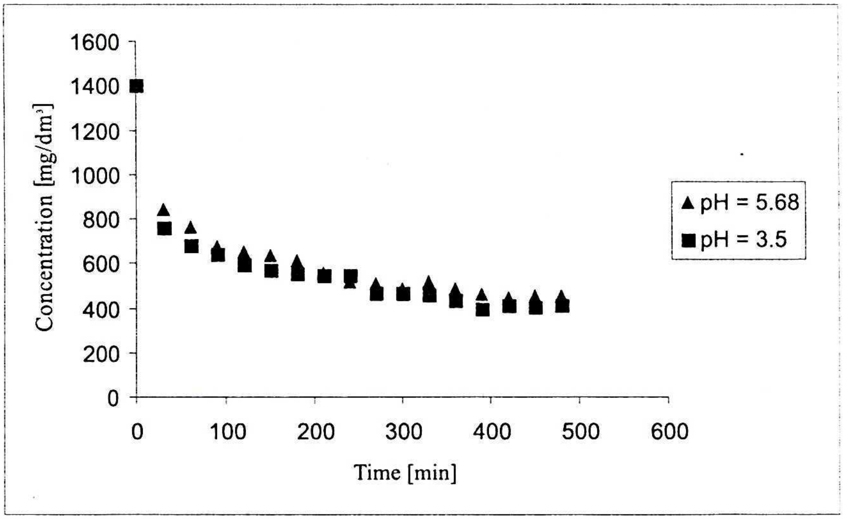

Fig. 4. Cr(VI) removal kinetic curve in flow condition

Kinetic model of adsorption

Experiments were performed in order to understand the kinetics of chromium removal on GFH. It is shown in Figure 5. The rate constant k, shown in Table 1 can be evaluated by the following pseudo-first-order expression:

$$dq/dt = k_{ad} (q_e - q) \qquad (5)$$

Integrating equation (5) for boundary from time t = 0, and if at the time t the concentration falls to q, it gives:

$$\lg (q_e - q) = \lg q_e - (k_{ad}/2.303)t \qquad (6)$$

Table 1. The rate constant for reaction values on different dosage GFH

pH	The rate constant for reaction, k [1/h]	R^2
5.86	0.39	0.97
3.5	0.31	0.95

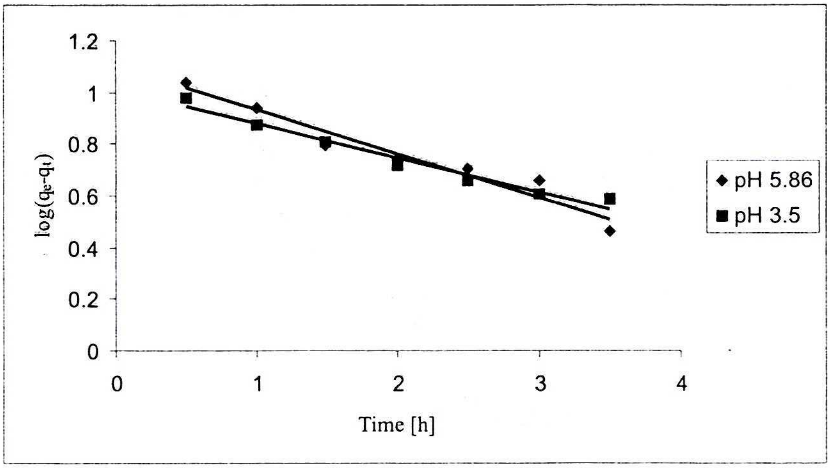

Fig. 5. Kinetic of Cr(VI) removal on ion-exchange resin Amberjet 4200 Cl

Intraparticle diffusion model

The rate constant for intraparticle diffusion kid can be evaluated by the following:

$$q = k_{id}\, t^{1/2} \tag{7}$$

It is shown in Figure 6 and Table 2.

Table 2. The rate constant for reaction values on different dosage GFH

pH	The rate constant for intraparticle diffusion, k_{id}	R^2
5.86	4.08	0.96
3.5	6.30	0.98

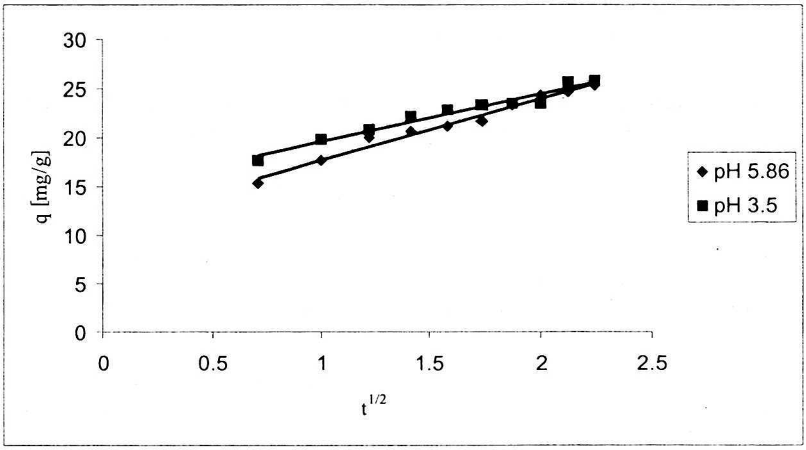

Fig. 6. Linear isotherm plot for the ion exchange of Cr(VI)

Adsorption capacity and desorption

To measure the adsorption capacity for GFH the adsorption column was operated until the column capacity was exhausted (i.e. concentration in the influent C_e was similar to the concentration in the inflow). It is shown in Figure 7. The GFH sorption capacity is 25 mg Cr/g of GFH.

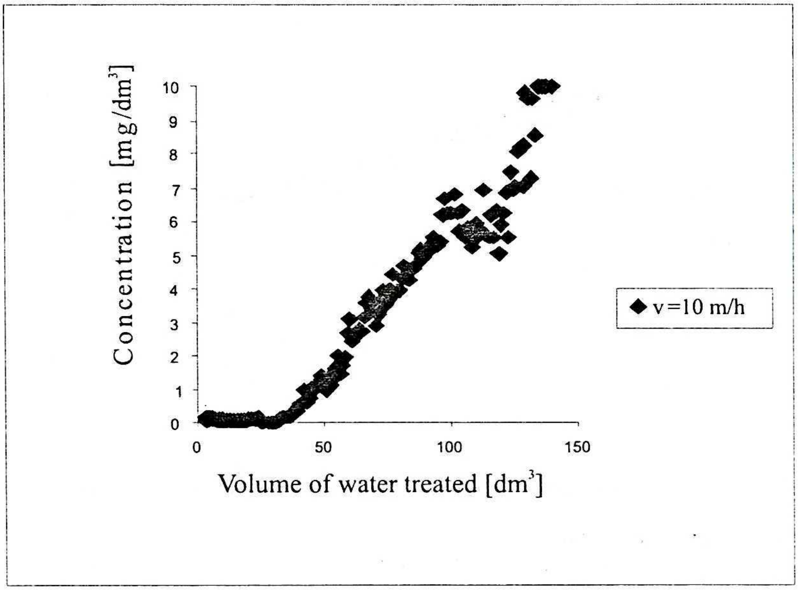

Fig. 7. Final concentration of Cr(VI) after sorption on GFH column

CONCLUSION

GFH is an effective adsorbent for Cr(VI) removal, with relatively high adsorption capacity.

Lower pH values would be advantageous for adsorbent in terms of the possible loading. Small specific amount of residuals can be easily disposed of without additional treatment.

During long-term operation contamination growth and clogging of adsorption filters might occur. At this point a regeneration procedure might replace backwashing.

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USUWANIE Cr(VI) Z ROZTWORÓW WODNYCH PRZEZ SORPCJĘ NA GRANULOWANYM WODOROTLENKU ŻELAZA (GFH)

W pracy przebadano efektywność sorpcji chromu(VI) na granulowanym wodorotlenku żelaza (GFH) w warunkach objętościowych i przepływowych. Badano skuteczność sorpcji zależnie od pH, czasu kontaktu i dawki adsorbentu. Pojemność sorpcyjną GFH zmierzoną w badaniach ekstrapolowano wykorzystując równanie izotermy Freundlicha. Pojemność ta wynosiła 25 mg/g. Jony metali zaadsorbowane na GHF mogą być z niego wymyte roztworem alkalicznym, co umożliwiałoby recyrkulację adsorbentu. Kinetyka wymiany jonów chromu na GFH może być opisana równaniem pierwszego rzędu. Kryterium limitującym wymianę jest dyfuzja międzycząsteczkowa. Wyniki wykazały praktyczną przydatność tej metody w przemyśle i stanowiły dowód na poparcie tezy wyjaśniającej mechanizm adsorpcji.