

## **SORPTION OF Cr(VI) FROM AQUEOUS SOLUTION BY PEAT**

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### **ABSTRACT**

*In this paper, the adsorption of Cr(VI) from aqueous solutions on Thua Thien-Hue peat was studied under both equilibrium and dynamic conditions in the concentration range of 2.5 - 10 mg/L. The peat was characterized by XRD, IR and isotherms of adsorption/desorption in nitrogen. The Cr(VI) was analyzed spectrophotometrically using diphenyl carbazide as a complexing agent. The adsorption of Cr(VI) was found to be pH dependent. The adsorption data could be fitted to Freundlich adsorption isotherm. The adsorption process was endothermic in nature. The effect of various doses of peat was also discussed.*

### **I - INTRODUCTION**

The chromium present in industrial wastewaters is mainly in the hexavalent form as chromate and dichromate. Cr(VI) is much more toxic than Cr(III) and its discharge to surface water is regulated to below 0.05 mgL<sup>-1</sup> by US EPA [1]. In view of the pollution hazards caused by Cr(VI), several methods of removal have been reported including chemical precipitation, reverse osmosis, ion exchange, foam flotation, electrolysis and adsorption. Among all the above-mentioned methods, adsorption is an economically feasible alternative due to easy operation and development of various cheap adsorbents. A variety of materials are used as adsorbent for Cr(VI) and various studies have been published documenting its adsorption on activated carbon obtained from different waste materials, biomaterials, hydrotalcite [2] etc.

Peat is a polar, highly porous material that could have significant application as an adsorbent for removal of heavy metals from aqueous solution. Peat contains lignin and cellulose. Functional groups in lignin that include alcohols, aldehydes, ketones, acids,

phenolic hydroxides, and ethers allow it to bind with various metal ions. Several studies have established the potential of peat to capture dissolved metals, nutrients, suspended solids, organic matter, oils and odors from domestic and industrial effluents [3]. In the present study, the material used, peat which has high reserves in Thua Thien-Hue province. Here, an attempt was made to study its feasibility as an adsorbent for removal of Cr(VI) from aqueous solution. Adsorption efficiency was investigated as a function of pH, time, concentration of adsorbate, amount of adsorbent and temperature.

### **II - EXPERIMENTAL**

Peat used as an adsorbent was collected from Huong Tra district, Thua Thien-Hue province. After removal of raw material, it was dried at 60°C for 1 h in an oven to remove the adhering moisture. The dried material was crushed to powder. The size of powdered material was classified by mesh sieves [3]. A textural property of peat was determined by nitrogen adsorption/desorption isotherms using Micromeritics at 77 K. The phase composition

of peat was identified by X-ray diffraction (XRD), recorded on 8D Advance Bucker, Germany with  $\text{CuK}\alpha$  radiation. The functional groups were determined by IR (JACO 670 Plus).

All the reagents used in this study were of analytical grade. Aqueous solution of Cr(VI) was prepared by dissolving requisite amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  in double distilled water. A stock solution having concentration 1000 mg/l of Cr(VI) was prepared and subsequently diluted to the required strengths to carry out the adsorption studies. The pH of the solution was varied using dilute hydrochloric acid and sodium hydroxide solutions. Adsorption studies were carried out in batches using 100 ml of Cr(VI) solution taken in 500 ml beaker with mechanical stirring where the temperature can be maintained within  $\pm 0.5^\circ\text{C}$ . For higher temperatures, the adsorption studies were carried out in a sealed unit to avoid the evaporation loss. Five millilitres of representative samples were drawn from the reaction mixture at regular interval and filtered. The residual Cr(VI) concentration was analyzed spectrophotometrically using diphenyl carbazide in a PE LAMBDA 35 UV-vis spectrophotometer [4].

In the batch adsorption process Cr(VI) solution of known concentration was agitated with peat in an incubator. The adsorption capacity ( $q_t$ ) was calculated using the Eq. (1)

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (\text{mg/g}) \quad (1)$$

where  $C_0$  and  $C_t$  are Cr(VI) concentration (mg/L) at initial time and the time recorded;  $V$  the volume of solution (L) and  $m$  weight of the adsorbent (g).

Kinetics of Cr(VI) sorption was modeled by the pseudo first-order, pseudo second-order equations presented below as Eqn. (2)-(3), respectively [4]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $q_e$  and  $q_t$  are the adsorption capacities (mg/g) at equilibrium at time recorded, respectively;  $C_e$  is the Cr(VI) concentration at

equilibrium;  $k_1$  is the pseudo first-order rate constant of adsorption ( $\text{min}^{-1}$ );  $k_2$  the pseudo second-order rate constant of adsorption ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ).

The isotherm of Cr(VI) adsorption was analyzed using the Freundlich and Langmuir [4].

The Freundlich equation is linearized in the form:

$$\ln q_e = \ln K_F + \frac{1}{n} C_e \quad (4)$$

where  $C_e$  is equilibrium concentration of Cr(VI) (mg/L);  $K_F$  and  $n$  are parameters of sorption capacity and sorption intensity, respectively.

The Langmuir equation is linearized in the form:

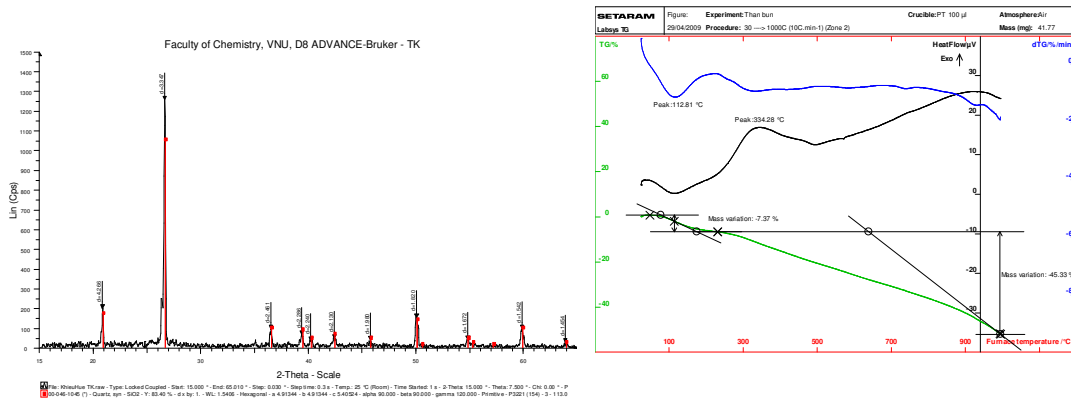
$$\frac{1}{q_e} = \frac{1}{b q_m C_e} + \frac{1}{q_m} \quad (5)$$

where  $q_m$  is the maximum capacity of adsorption (mg/g) and  $b$  is a constant related to the affinity of the binding sites (L/g).

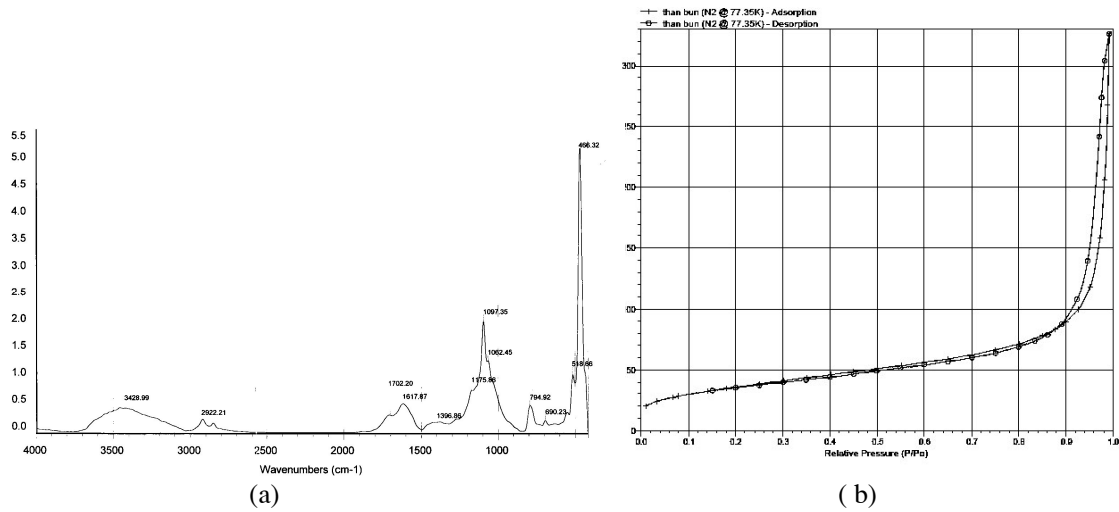
### III - RESULTS AND DISCUSSION

The phase composition of peat were investigated by XRD (Fig. 1a). No reflection was observed excepted for characteric reflections of quazt indicating that the peat consists of large amount of quazt and amophous phase. The thermal behavious of peat was presented at Fig 1b. The exothemic peak at  $334^\circ\text{C}$  corresponding to large ignition loss of 45% should be attributed to oxidation/decomposition of organic compositions. It is clear that the remain around 55% at more  $900^\circ\text{C}$  is related to inorganic compounds. Fig. 2a shows IR spectrum of peat. A dertermination of the peaks in spectrum of the main functional groups was based several publications [5, 6].  $3500 - 3300 \text{ cm}^{-1}$  zone is related to OH stretch. The band of  $3000 - 2800 \text{ cm}^{-1}$  revealed an aliphatic carbon CHx stretch. In addition, the carbonyl stretching vibration of carboxylic acid  $\text{C}=\text{O}$  at  $1770 \text{ cm}^{-1}$  and ketone carboxyl band  $\text{C}=\text{O}$  at  $1689 \text{ cm}^{-1}$  were determined. A  $\text{C}=\text{C}$  stretch at  $1470 - 1511 \text{ cm}^{-1}$  that may indicate the presence of aromatic ring carbons [5]. C-O-R structures of ethers were observed at  $1080 \text{ cm}^{-1}$ . The textural

properties of peat were also studied by nitrogen adsorption isotherm.



(a) (b)  
Fig. 1: (a) XRD pattern and (b) TG-DCS curves of peat



(a) (b)  
Fig. 2: (a) IR spectrum and (b) isotherms of adsorption/desorption of nitrogen

Fig. 2b gives the adsorption and desorption isotherms of  $N_2$  at 77 K on peat sample. The obtained curve is the isotherms of III type, its shapes is typical of macroporous materials. This sample exhibits one well-expressed hysteresis loop at  $P/P_0 > 0.4$  corresponds to capillary condensation in the inter-particle pores. The nitrogen physisorption at low relative pressure ( $P/P_0 < 0.3$ ) is usually assigned to monolayer adsorption. Therefore the data collected in this part of the isotherm are

used for the calculation of surface area of material with BET method [7]. Thus calculated surface area around  $124 \text{ m}^2/\text{g}$  for the present peat is very high compared with some other natural minerals

Fig. 3 shows the effect of solution pH on the uptake of Cr(VI) by peat. In the the range of pH from 1.8 - 10.5, it is clear that the adsorption capacity decrease with the increase in pH. In this range of pH, Cr(VI) is in the form of  $\text{Cr}_2\text{O}_7^{2-}$ ,

$\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ . Thus  $\text{OH}^-$  could compete with the Cr(VI) species for sorption sites. Sorption of excess of  $\text{OH}^-$  ions could convert an initial positively charge surface of peat into negatively charged surface resulting repulsion of negatively charged Cr(VI) ions and adsorption decreased.

According Fig. 3b, Cr(VI) uptake is relatively fast for all the concentration studied. At initial Cr(VI) concentration in range from 2.5 - 10 mg/L, the system reached to equilibrium within 90 min. Kinetic parameters of kinetic modeling of Cr(VI) adsorption were shown in table 1 The pseudo

second-order described the adsorption with high correlation coefficient ( $R^2 > 0.99$ ) and better than the pseudo-first order equation. The rate constants of the pseudo second-order rate equation for Cr(VI) adsorption were obtained 1.101, 0.755 and 0.349 mg/g.min at initial Cr(VI) concentrations of 2.5, 5 and 10 mg/L, respectively. The theoretical  $q_e$  values ( $q_{e,theo}$ ) were closer to the experimental  $q_e$  values ( $q_{e,exp}$ ). In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the adsorption of Cr(VI) onto peat in contrast to the first-order-model.

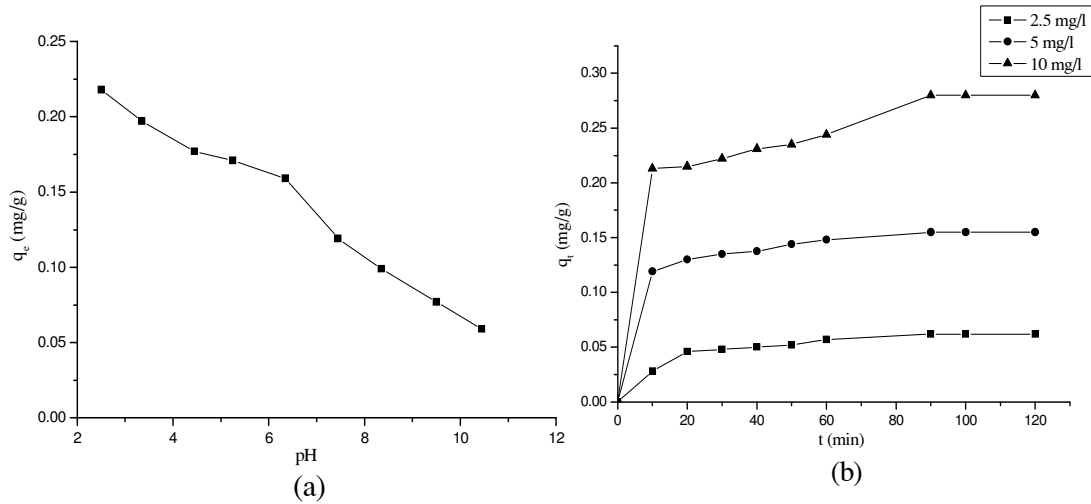


Fig. 3: (a) Plot of the adsorption capacity vs pH and (b) Plot of the adsorption capacity vs time

Table 1: The kinetic parameters predicted by using three mentioned models and correlation coefficients ( $t = 25^\circ\text{C}$ , 2 g peat/100 mL Cr(VI) solution, initial pH = 4 - 5)

| Kinetic model  | Parameter    | Initial concentration of Cr(VI) ion (mg/L) |       |       |
|--|--------------|--|-------|-------|
|  |              | 2.5  | 5     | 10    |
| Pseudo-first-order<br>$\ln(q_e - q_t) = \ln q_e - k_1 t$                       | $k_1$        | 0.037                                      | 0.034 | 0.026 |
|  | $R^2$        | 0.936                                      | 0.868 | 0.796 |
|  | $q_{e,exp}$  | 0.060                                      | 0.140 | 0.280 |
|  | $q_{e,theo}$ | 0.07                                       | 0.150 | 0.300 |
| Pseudo-second-order<br>$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ | $k_2$        | 1.101                                      | 0.755 | 0.349 |
|  | $R^2$        | 0.997                                      | 0.997 | 0.992 |
|  | $q_{e,exp}$  | 0.060                                      | 0.140 | 0.280 |
|  | $q_{e,theo}$ | 0.07                                       | 0.150 | 0.300 |

Table 2 shows isotherm parameters of Cr(VI) adsorption by linear plots of Freundlich and Langmuir. Isotherm data are basic requirements for the design of adsorption reactors, moreover analysis of adsorption isotherm is important to develop an equation which accurately represents the results and which can be used for design purposes. The Freundlich model described the isotherm of Cr(VI) adsorption with high correlation coefficient ( $R^2 > 0.94$ ) and better than Langmuir model. In fact,

Langmuir equation is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute on the adsorbent surface, that energy of adsorption is constant in changing adsorption coverage ( $\theta$ ) and that there is no transmigration of adsorbate in the plane of the surface while the empirical Freundlich model based on sorption on a heterogeneous surface. Hence, this is compatible with the fact that peat possesses "rough" surfaces.

Table 2: Isotherm parameters of Cr(VI) adsorption by peat

| Langmuir model (Linearized shape) |                    |       | Freundlich model (Linearized shape) |       |       |
|-----------------------------------|--------------------|-------|-------------------------------------|-------|-------|
| $q_m$ (mg/g)                      | $\square_L$ (mg/L) | $R^2$ | $n$                                 | $K_f$ | $R^2$ |
| 0.409                             | 0.687              | 0.858 | 1.801                               | 0.158 | 0.97  |

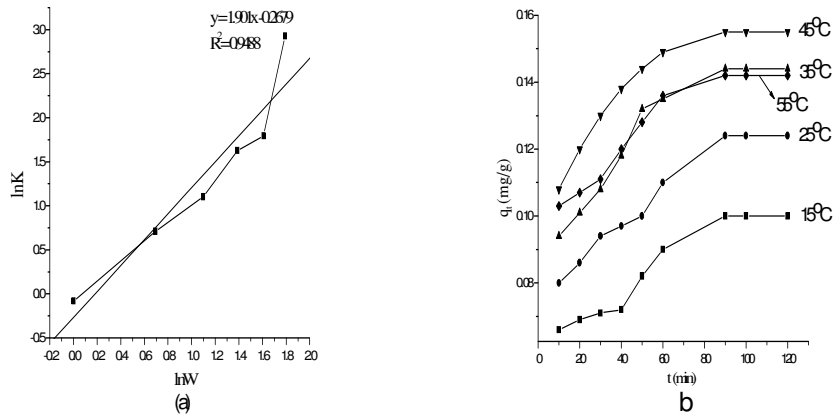


Fig. 4: (a) The relationship  $\ln k - \ln W$  and (b). Effect of temperature on the adsorption of Cr(VI) on to peat

The effect of varying doses of peat was investigated using 5 mg/L of initial Cr(VI) concentration at initial pH 2 - 3. It shows an increase in degree of adsorption of Cr(VI) with the increase in dose of adsorbent ( $W$ ) up to a certain limit ( $\approx 5$  g/100 mL) and then it remains almost constant. An increase in the degree of adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites.

The relationship between the rate constants of Cr(VI) ion adsorptions and the doses of peat used as adsorbent ( $W$ ) can be expressed as follows [8]:

$$k = k_0 W^n \quad \text{or} \quad \ln k = \ln k_0 + n \ln W \quad (6)$$

where  $k$  is the rate constant of the pseudo-second-order adsorption (g/mg.sec),  $k_0$  is a coefficient,  $n$  is the adsorption order with respect to adsorbent amount.

In case of  $W > 5$  g/100 mL, the rate of adsorption is almost independent of dose of adsorbent, thus,  $n = 0$ . In the ranges  $W \approx 5$  g/100 mL, linearizing the experimental data of  $\ln k$  and  $\ln W$  (Fig. 4a) can determine the adsorption order with respect to the value  $n \sim 1.9$ . This result is also agreement with the conclusion on the satisfaction of the adsorption Cr(VI) on peat with the pseudo- second-order kinetic model ( $n = 2$ ).

Fig. 4b represents effect of temperature on degree of adsorption of Cr(VI) on to peat. It can be seen an increase in degree of adsorption with increase in temperature. It proved that the adsorption is a endothermic process in the range of studied temperature (15 - 45°C). With temperature in range from 45 - 55°C, the increase in degree of adsorption is negligible. It indicates that the degree of adsorption has reached maximum in this range of temperature. However, when temperature reached to 55°C, the degree of adsorption reduced remarkably. It can be due to at higher temperature the adsorption was limited by the intra-particle diffusion process, at that time the rate of adsorption was decreased and the rate of desorption was increased. The desorption process was not to mention in this paper.

### III - CONCLUSIONS

The adsorption of Cr(VI) on to peat followed a pseudo-second order reaction. The Freundlich model was found to be the best describing the data of Cr(VI) ion sorption on to peat. Results of investigation into effect of

temperature on the degree of adsorption showed that the adsorption degree of Cr(VI) ion on to peat reach to maximum value in range temperature 30 - 35°C. Effect of adsorbent dose was also observed, it indicated that the adsorption order with respect to value  $n \sim 1.8$ . The adsorption dependence of Cr(VI) on temperature was investigated indicating that the process of Cr(VI) adsorption is favored at high temperatures.

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