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International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.12, pp 4964-4969, October 2014

CBSE-2014 [2nd and 3rd April 2014]

Challenges in Biochemical Engineering and Biotechnology for Sustainable Environment

Adsorption of Chromium (VI) From Aqueous Solution onto Bio-Organic Waste in Batch Reactors – An Equilibrium Study

P. Mullai[1], S. Kothai Nayaki[2], M. K. Yogeswari[1] and R. Nirmala[2]

[1]Department of Chemical Engineering, [2]Department of Chemistry, Faculty of Engineering and Technology, Annamalai University, Annamalai Nagar-608 002, India.

***Corres.author : pmullai@yahoo.in**

Abstract : The presence of heavy metals in water supplies and wastewater threatens the environment and the health of humans. The adsorption of chromium (VI) onto cowdung ash, a bio-organic waste was investigated in a batch reactor under two different conditions, namely, initial metal ion concentration and adsorbent dosages. For the five different initial metal ion concentrations such as 500, 600, 800, 900, 1000 mg/L, the steady state values of chromium removal efficiency were 100, 83.33, 88.09, 94.3 and 96 %, respectively, using 20 g of cowdung ash under shaking at the end of 3rd h. The equilibrium of the process was found to fit into the two well-known adsorption models, Freundlich and Langmuir. The results obtained in this study revealed the potential application of the cowdung ash in the removal of metal ions from the aqueous solution.
Keywords: Hexavalent chromium removal, Bio-organic waste, Langmuir and Freundlich equilibrium models.

Introduction

The presence of heavy metals in water supplies and wastewater threatens the environment and the health of humans. Chromium naturally occurs in the environment as chromium (III) or chromium (VI). Chromium toxicity and mobility depend on its oxidation state. The trivalent forms are relatively immobile, more stable, and much less toxic than the hexavalent forms[1]. Chromium (VI) contamination is particularly imperative to remediate because of the severe carcinogenic and toxic effects on humans and fauna[2, 3]. Much has been reported on the treatment of chromium bearing effluents. Traditionally, chromium removal is made by chemical precipitation. However, this method is not completely feasible to reduce chromium concentrations to levels as low as required by environmental legislation. Adsorption is a promising alternative method to treat the industrial effluents containing chromium mainly because of its low cost and high metal binding capacity. Particularly, adsorption onto activated carbon has been a useful and effective process for purification of industrial wastewaters and for advanced treatment of effluent from biological treatment plants[4]. But, it is quite costly. Therefore, many research workers have tried to investigate the usefulness of commonly available cheap materials like saw dust[1], rice husk ash[5], rice straw[6], sewage sludge[7] and cowdung ash[8, 9, 10]. Cowdung ash, a bio-organic waste, contains calcium oxide 12.48%, magnesium oxide 0.9%, calcium sulphate 0.312%, aluminium oxide 20%, iron oxide 20% and silica 61%[8]. The presence of maximum percentage of silica exhibits considerable affinity for metal ions. The metal binding capacity of cowdung ash for chromium is important in designing adsorption contacting systems. The aim of the present work is to determine the adsorption capacity of cowdung ash for hexavalent chromium in aqueous solution.

Materials and Methods

Adsorbent

Cow dung ash was procured from the local village and powdered using pestle and mortar to a geometric mean particle size of 100 mesh (B.S.S).

Preparation of synthetic effluent

In order to have waste of uniform characteristics and to avoid interference with other elements the synthetic effluent for the present study was prepared by dissolving known amount of potassium chromate (K_2CrO_4) in distilled water. For 1000 mg/L hexavalent chromium concentration 3.7349 g AR grade K_2CrO_4 was dissolved in 1.0 L of distilled water.

Experimental procedure

Batch reactors were employed in carrying out the experiments. 100 mL of the synthetic effluent with known quantity of cowdung ash were added to the 250 mL batch reactors and agitated continuously in a rotary shaker and the temperature was maintained at 30ºC. The samples were removed at regular time intervals, filtered with Whatmann filter paper No. 44 and the filtrate was analysed for its residual chromium (VI) concentration. The experiments were carried out to study the effect of operational parameters like initial metal ion concentrations and adsorbent dosages. The equilibrium study was carried out by varying the initial metal ion concentration and by keeping the temperature constant.

Analysis of chromium (VI) ions

The concentration of unadsorbed chromium (VI) ions was analysed spectrophotometrically at 540 nm using diphenyl carbazide as the complexing agent by following the standard procedure given by APHA[11].

Results And Discussion

Effect of contact time

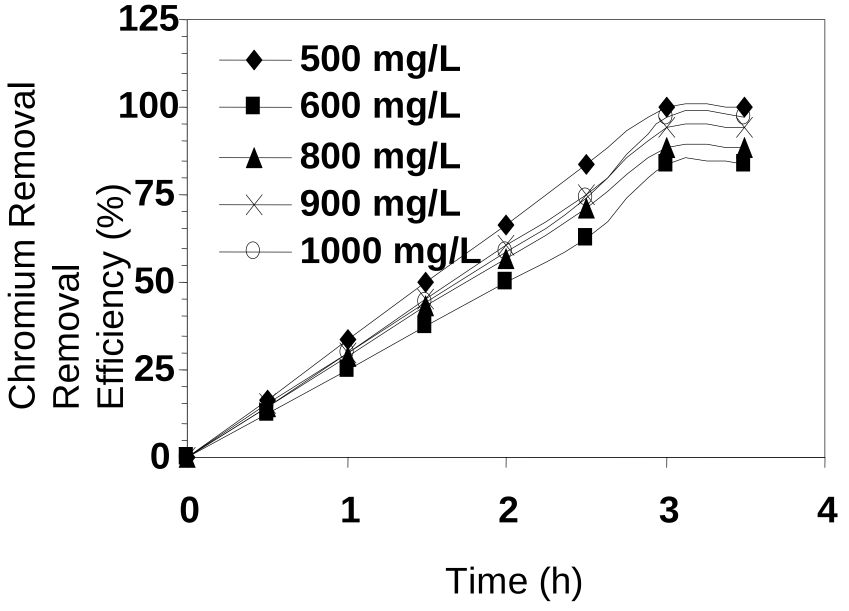

Fig. 1 Effect of contact time on chromium removal efficiency

In the adsorption system, contact time plays a vital role irrespective of other experimental parameters affecting the adsorption kinetics. In the present study, the experiments were performed by varying contact time and found that the adsorption of Cr (VI) increased with increase in contact time irrespective of initial concentration of hexavalent chromium (Fig. 1). The equilibrium was attained at the end of 3rd h. The metal was removed due to adsorption by 20 g of cow dung ash. Similar results were made by Viswanadham et al.[12] and Hameed et al.[13] in their work on removal of zinc and nickel ions using a biopolymer, chitin and 2,4 D pesticide on activated carbon derived from date stones. In disparity, Monser and Adhoum[14] reported that a large fraction of tartrazine was removed in 20 mins.

Effect of initial concentration

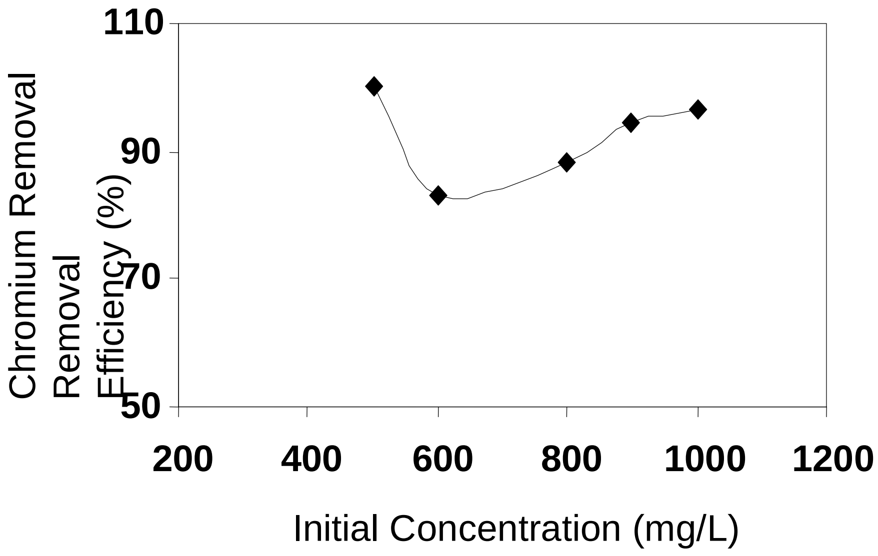

Fig. 2 Effect of initial concentration on chromium (VI) removal efficiency

The five different initial concentrations of synthetic chromium effluent such as 500, 600, 800, 900 and 1000 mg/L, the metal removal efficiencies were 100, 83.33, 88.09, 94.3 and 96.72 % respectively, using 20 g of cow dung ash at the end of 3rd h (Fig. 2). The metal removal efficiency was 100% for 500 mg/L due to low concentration of effluent. The amount of chromium adsorbed per unit weight was maximum at lower concentration and minimum for higher concentrations[15]. Vasantha Kumar and Bhagavanalu[8] reported similar finding in their work on adsorption of basic dye from its aqueous solution on bio-organic waste.

Effect of adsorbent dosage

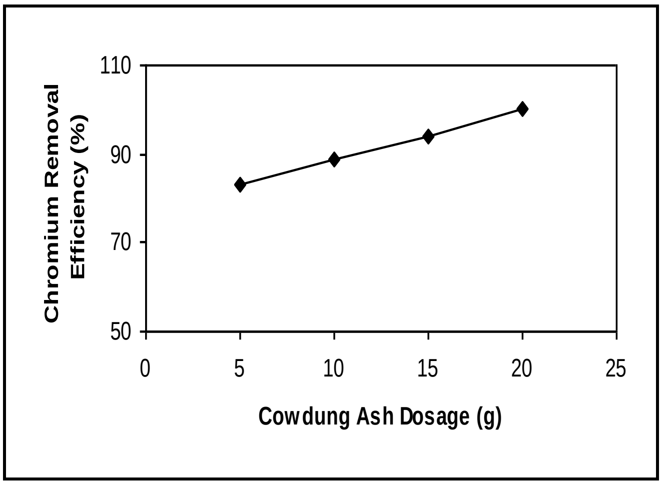

Fig. 3 Effect of cowdung ash dosage on chromium removal efficiency

The experiment was conducted for the different dosage values of cow dung ash such as 5, 10, 15 and 20 g for the initial chromium concentration of 500 mg/L. The equilibrium metal removal efficiency values at the end of 3rd h were 83.33, 88.88, 94.11 and 100% respectively (Fig. 3). Increase in adsorption of metals with increase in adsorbent dosages could be ascribed to availability of more active adsorbing sites. Findings akin to this study were reported by Nirmala et al.[16] and Akhtar et al.[17] in their work on the removal of hexavalent chromium using industrial waste biomass and organophosphorus pesticides onto chickpea husk respectively.

Equilibrium study

Analysis of equilibrium data is important for design purpose in developing an equation describing the process. For equilibrium modeling of the adsorption systems, the equilibrium data obtained was fitted with the two well known adsorption models, Langmuir and Freundlich models, using their linearized forms.

The Langmuir isotherm model is expressed as,

$$q_e = \frac{Q^o b C_e}{1 + bC_e} \quad \ldots \quad (1)$$

where

q_e (mg/g) and C_e (mg/L) are the amount of metal ion per unit weight of adsorbent and unadsorbed metal ion in solution at equilibrium, respectively.

Q° (mg/g) is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer on the surface and

b (L /mg) is a constant related to the affinity of the binding sites.

The Freundlich isotherm is based on the heterogeneous surface is expressed as

$$q_e = K_F C_e^{1/n} \quad \ldots \quad (2)$$

where K_F and n are the Freundlich constants. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively.

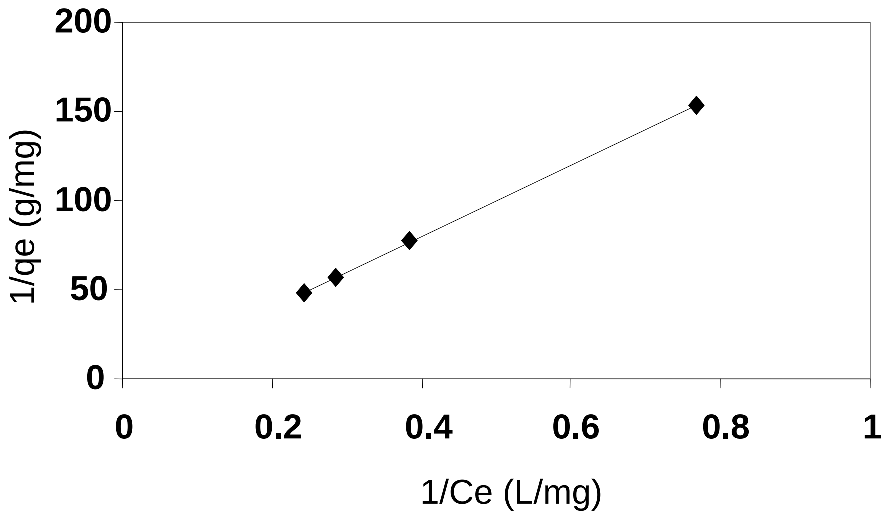

Fig. 4 Langmuir plot for the adsorption of chromium by cowdung ash

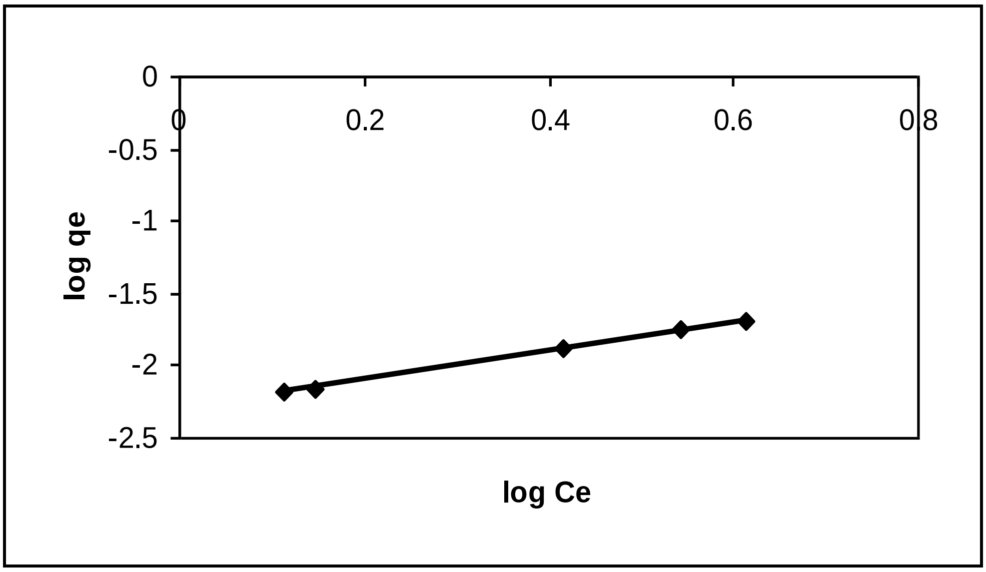

Fig. 5 Freundlich plot for the adsorption of chromium by cowdung ash

The experimental data were found to fit with the Langmuir and Freundlich isotherms (Figs. 4 and 5). The Langmuir and Freundlich adsorption constants were evaluated from the isotherms. The isotherm constants values of Q°, b, K_F and n were 29.1 (mg/g), 0.4582 (L/mg), 0.005 (L/g) and 1.001, respectively. Q° (mg/g) is important to identify the highest uptake and the value of b implies the strong bonding of Cr (VI) to cowdung ash at these experimental conditions[18].

The essential characteristics of Langmuir isotherm can be described by a separation factor[19] which is defined by, $R_L = \frac{1}{1+bC_i}$. Since R_L value lies between 0 and 1, the reported isotherm represents the favourable adsorption. According to Treybal[20], the values n >1 represent favourable Freundlich isotherm adsorption condition and the same was obtained in the present investigation. Furthermore, the higher correlation coefficients showed that both the Freundlich and Langmuir models are very suitable in describing the adsorption equilibrium of the metal by cowdung ash in the studied concentration range. Similarly results were observed by Iftikhar et al.[21] and Barkat et al.[22] during their studies on adsorption of Cu (II) and Cr (III) using rose waste biomass and Cr (VI) ions using activated carbon respectively.

Conclusions

The results obtained in this study revealed the potential application of the cowdung ash in the removal of metal ions from the aqueous solution. The equilibrium time was found to be 3 h. The equilibrium of the process was fitted into the two well-known adsorption models, Freundlich and Langmuir.

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