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Adsorptive removal of chromium (VI) by chemically activated agricultural waste sugarcane bagasse

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ABSTRACT - The ability of chemically modified sugarcane bagasse for the removal of Cr (VI) from aqueous solution was investigated as a function of change in pH at temperature 28±1ºC, concentration 1.987×10^{-4} M and particle size <55 mm. The adsorption of Cr (VI) on chemically modified bagasse (MB) was nearly 8% higher against unmodified bagasse (UB). The acidic pH of the medium promoted the rate of Cr (VI) adsorption on the adsorbent while inhibited at neutral or alkaline pH and gave good fit for adsorption kinetics equation.

Key words - Sugarcane bagasse, Adsorption, Chemically activated, Adsorbents, Chromium (VI)

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Toxic metals release into the environment has been increasing continuously as a result of man's activities which posses a significant threat to environmental quality and public health. Several episodes due to heavy metal contamination in aquatic environment increased the awareness about the heavy metal toxicity. Among these, minimata and *itai-itai* due to mercury and cadmium, respectively, in Japan are well known. Chromium (VI) compounds are toxic which can even cause lung cancer, often used in metal processing, electroplating, leather tanning, paints and pigments, canning industries, wood preservatives etc. Chromium is discharged, from there industries as in waste water effluents.

A number of techniques have been reported in literatures to reduce the heavy metal ions from waste water effluents (Deitz, 1956; Dean *et al*. 1972; Braukmann, 1990). These methods have been found to be limited, since they are often involved high capital and optimal cost and may be associated with generation of secondary wastes. On the other hand agricultural products and byproducts are an abundant waste material and need proper disposal. The idea of using various agricultural products and byproducts, available a little or no cost due to waste products for the removal of heavy metals from solution has been investigated by a number of investigators (Khawas and Dara, 1994; Egila and Okore, 2002; Saraswathi *et al*., 2009; Singh and Pandey, 2011). Ligmin based materials were also investigated for cation (Garg and Sud 2005, Singh and Pandey, 2012). The present work describes the batch adsorption characteristics of Cr (IV) on chemically modified sugarcane bagasse at different pH for the removal of Cr (VI) from aqueous solution were investigated.

EXPERIMENTAL METHODOLOGY

Preparation of adsorbent:

Sugarcane bagasse was obtained formers of local area and boiled with water for 30 minutes to removal the soluble sugar. Boiled bagasse was dried at 120ºC in a hot air even for 24 hrs. Dried material was ground and seined. Seived bagasse was treated with 0.1M citric acid for 24 hrs for chemical modification and then washed with double distilled water. After washing chemically treated bagasse powder was dried for a constant weight.

Preparation of solution for adsorption:

A stock solution of Cr(VI) was prepared by dissolving 2.8287 g of $K_2Cr_2O_7$ in 1000 ml of distilled water. The solution was diluted to obtained standard solution containing 1.987×10^{-4}M concentration of Cr(VI).

Batch experiment:

100 ml of 50 mgl^{-1} chromium solution was taken in 250ml flask and pH 4, 5, 6 and 7 was adjusted by using 0.01 N NaOH or 0.01 N HCl. A known amount (0.5 g) of unmodified and modified sugarcane bagasse were added to each flask containing Chromium (VI) solution and agitated in a shaker for the different contact time (10, 20, 30, 40, 60, 80, 100 and 120 min.). After each agitation time, the content from each flask was taken and filtered. The residual concentration of 20 ml of the filtrate of each metal solution was analysed spectrophotometrically against blank. Temperature, particle size and concentration of the adsorbent was kept constant at different pH. Selected adsorbent particle size was based on highest adsorption efficiency. Adsorption dynamics was calculated by taking adsorption rate constant and first order reversible reaction kinetics was used for the rate of reaction (Helfterich 1962; Singh *et al*. 1987).

EXPERIMENTAL FINDINGS AND ANALYSIS

Partial composition of the sugarcane bagasse is given in Table 1 (Garg and Sud 2005). Initial studies with sugarcane bagasse for chemical modification described elsewhere (Abia and Asuquo, 2006). Table 2 and 3 represent the chromium (VI) removal as a function of bagasse over pH range 4 to 7 for both unmodified (UB) and modified (MB). The change in pH of the solution has no effect on the basic nature of the time growth adsorption curves and saturation periods. However, the extent and rate of adsorption vary significantly with change in pH of the medium and modification of the adsorbent. The adsorption of Cr(VI) on unmodified (normal) adsorbent, sugarcane bagasse (UB). The extent of removal changes from 75% (0.375 mg g^{-1}) to 34.0 % (0.170 mg.g^{-1}) and adsorption rate constant (k_1) from 0.0374 min^{-1} to 0.01952 min^{-1} at pH 4 and 7 respectively with optimum velocity at pH 4. However, the percent adsorption was significantly increased with chemically modified sugarcane bagasse (MB) at the same pH (Table 2 and 3). The adsorption was decreased from 85.2% (0.426 mg.g^{-1}) to 37.2% (0.186 mg.g^{-1}) at pH 4 and 7 respectively with adsorption rate constant 0.0374 min^{-1} to 0.01952 min^{-1}. Over all rate constant (k_1) and rate constant of adsorption (k_1) at different pH for both adsorbent was calculated and results were presented in Table 4.

Table 1 : Partial composition of the sugarcane bagase (% w/w dry matter) (Garg and Sud, 2005)

Total reducing sugar	70.9
Xylose	25.2
Glucose	41.0
Fermentable reducing sugar	46.6
Non-fermentable reducing sugar	26.3
Lignin	23.0
Ash	1.1
Moisture (% w/w of the wet matter)	47.8

Table 2 : Effect of pH on adsorption of Cr(VI) by sugarcane bagasse (unmodified/UB) at different time intervals (Temp 28±1°C, Concentration 1.987×10^{-4} M, Particle size < 55 μm)

Time (min)	Amount adsorbed (mg g^{-1}) pH 4	5	6	7
10	0.148	0.110	0.075	0.035
20	0.198	0.175	0.125	0.070
30	0.245	0.230	0.168	0.098
40	0.290	0.276	0.210	0.122
60	0.33	0.315	0.240	0.140
80	0.355	0.340	0.264	0.155
100	0.365	0.352	0.278	0.162
120	0.375	0.365	0.290	0.170
140	0.375	0.365	0.290	0.170

Table 3 : Effect of pH on adsorption of Cr(VI) by sugarcane bagasse (modified, MB) at different time intervals. (Temp 28±1°C, Concentration 1.987×10^{-4} M, Particle size < 55 μm)

Time (min)	Amount adsorbed (mg g^{-1}) pH 4	5	6	7
10	0.159	0.148	0.118	0.061
20	0.262	0.230	0.172	0.088
30	0.326	0.295	0.223	0.113
40	0.367	0.330	0.263	0.136
60	0.40	0.368	0.292	0.156
80	0.416	0.394	0.314	0.172
100	0.426	0.408	0.332	0.186
120	0.426	0.408	0.332	0.186

It is obvious from the results that pH of the medium affected the rate constant in accordance with extent of adsorption. The maximum adsorption has been noticed at pH 4 and thereafter, there is an exponential decrease in the extent of adsorption with increase in pH (4 to 7). At pH 4 where maximum uptake of Cr(VI) has been noted in both the conditions of the adsorbents, there exists a significantly high electrostatic attraction between protonated adsorbent surface and negatively charged adsorbate species. This results in a high driving force for the formation of surface complex or

Table 4 : Overall rate constant (k^1.min^{-1}) and rate constant of adsorption (k_1. min^{-1}) or Cr(VI) by chemically unmodified and modified sugarcane bagasse

Adsorbate	Adsorbent	Concentration mole l^{-1}	Temp.	pH	Over all rate constant k^1.min^{-1}	Rate constant k_1.min^{-1}
Cr (VI)	Sugarcane bagasse	1.987×10^{-4} M	28±1ºC	4	0.0484	0.0374
	chemically modified			5	0.0372	0.0348
	(MB)			6	0.0347	0.0314
				7	0.0301	0.0195
Cr (VI)	Sugarcane bagasse	1.987×10^{-4} M	28±1ºC	4	0.0355	0.0311
	chemically			5	0.0304	0.0293
	unmodified (UB)			6	0.0296	0.0285
				7	0.0288	0.0200

their presence as chromates on the surface adsorbents (Pandey *et al*., 1984). At pH around 4, there is a possibility of the dissolution of substrate and whose constituents cause surface precipitation of chromate. In acidic range the uptake of Cr(VI) by these adsorbents is expected due to the possibility of chromate ion exchange at solid solution interface. More adsorption of Cr(VI) by chemically modified bagasse might be due to increase in surface area which has great effect on sorption capacities of adsorbent (Abia *et al*., 2002, 2003; Quadeer and Aktar, 2005; Singh and Pandey, 2011).

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