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Sorption isotherms for decolourization and hardness removal from buddha drain effluent using acid activated carbons

Simmi Goel*, Bhavpreet Kaur
Department of Biotechnology, MataGujriCollege, Fatehgarh Sahib - 140 406, Punjab, (INDIA)
E-mail : simmig76@yahoo.co.in

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ABSTRACT

The use of rice husk and saw dust as a low cost natural adsorbent for decolorization and hardness removal from Buddha Drain waste effluent was studied. Batch experiments were conducted to determine the effects of varying adsorbent loading, pH, contact time, agitation speed and concentration of effluent on rate of adsorption. The % decolorization was found to be maximum (90-94%) at pH 2, contact time of 70-80minutes, agitation speed of 120rpm, sorbent dosage of 4g/100ml for both the biosorbents. Rice husk was found to be better sorbent as compared to sawdust in terms of color and hardness removal. Langmuir isotherm obtained from linear form of Langmuir 1 was found to be more suitable as compared to Freundlich isotherm for adsorption.

KEYWORDS

Adsorption;
Isotherms;
Activated carbon;
Decolorization;
Biosorbents.

INTRODUCTION

Buddha Drain runs parallel to the Satluj on its south for a fairly large section of its course in the Ludhiana district and ultimately joins the Satluj at Gorsian Kadar Baksh in the northwestern corner of the district. The only surface water body Buddha Drain, an unlined canal, is the main receptor of city's domestic and industrial sewage. The major industrial sources of water pollution in Ludhiana, Punjab include textile industry, Food Products, Card Board Mills, Rerolling Mills, Vegetable Ghee Mills, Chemical Industries, Arc, Cupola and Induction Furnaces. Buddha Drain wastewater also consists of heavy metals such as chromium, nickel, iron, lead, copper, silver, manganese etc. Natural biodegradable waste material from industrial and agricultural operation may have potential as inexpensive adsorbents. These include coir pith by Namasivayam et al.[1], Bagasse pith by Krishnan and Anirudhan[2], Cassava waste by Abia et al.[3], Soya cake by Gupta et al.[4], Eucalyptus bark by Sarin and Pant[5], and Tendu leaves by Nagda et al.[6]. Activated carbons from two different types of sugarcane wastes, agricultural residues and bagasse were prepared by phosphoric acid activation as shown by Castro and coworkers[7]. The aim of this research work was to investigate the use of low cost activated rice husk and sawdust in decolorization of effluent after optimizing certain factors like adsorbent loading, pH, contact time, agitation speed and concentration of effluent. The Freundlich and linear regression method for Langmuir adsorption isotherms were used to investigate the adsorption process.

MATERIALS AND METHODS

Procurement of effluent and activation of adsorbates Effluent was collected from Buddha Drain, Ludhiana, and Punjab (INDIA). Each type of raw carbon was washed with distilled water several times separately until the supernatant was colourless and dried at 70°C. The biomaterial was sieved to obtain a particle size range of 0.15-0.5mm. After complete drying, concentrated sulphuric acid and formaldehyde were added in ratio of 4:1.5. After acidification, carbon mixtures were kept in oven at 150°C for 12 hours. The char obtained was washed with distilled water and then soaked in 1% sodium carbonate to remove residual acid. Then char was washed with distilled water and then dried at 105°C for 24 hours.

RESULTS AND DISCUSSION

Effect of Hydrogen ion concentration, contact time, adsorbent loading and agitation speed % decolourization was observed to be maximum (91-93.5%) at pH 2 for both the activated carbons. The reason for the better adsorption capacity observed at pH 2 may be attributed to the larger number of H^+ ions present, which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of organics at higher pH. At higher pH, the capacity of the adsorbent recessed[8]. At 1 hour of contact time, maximum decolourization (90.5%) was achieved in case of saw dust and by increasing the contact time beyond 1 hour, the % decolourization was observed to be constant. In case of rice husk as activated carbon, maximum decolourization i.e. 93.2 % was achieved after 80 minutes beyond which it was found to be constant. Maximum decolourization was achieved at adsorbent dosage 4g/100 ml in case of both the sorbents. The increase in adsorption with increase in adsorbent dosages can be attributed to greater surface area, availability of more adsorption sites or due to conglomeration of carbons at higher doses[9]. Effluent was mixed with adsorbent at the rate of 4g/100 ml and kept on rotary shaker at various agitation speeds i.e. 100, 150 and 170 rpm. Rate of decolourization was increased with agitation speed in case of activated saw dust. This is due to the resistance to mass transfer, which mainly lie around the surface of adsorbents, breakdown with increasing agitation speed, as a result, more amount of colour compounds penetrate into the adsorbent, and optimized speed was observed at 150 rpm and 170rpm and beyond this, a slight decrease in colour removal was found. It can be depicted that RHAC was found to be better adsorbent in terms of color and hardness removal (93.5% and 62%) as compared to SDAC (90% and 53%) respectively.

TABLE 1 : Values of C_o, C_e, q_e, log C_e and log q_e for different effluent concentrations

Effluent conc.	Initial Hardness (C_o)	Equilibrium Hardness (C_e)	C_o-C_e	(C_o-C_e)/V	q_e	logq_e	logC_e
100%	460	310	150	1.5	0.375	-0.425	2.491
80%	320	200	120	1.2	0.3	-0.522	2.301
60%	210	100	110	1.1	0.275	-0.560	2.0
40%	180	80	100	1.0	0.25	-0.60	1.90
20%	120	60	60	0.6	0.15	-0.823	1.77

TABLE 2 : Various parameters obtained from Freundlich isotherm equation

Freundlich		
1/n	log K_f	r^2
0.5	1.1	0.776

TABLE 3 : Various parameters obtained from Langmuir isotherm equations

Isotherm	q_m	K_a	R_L	r^2
Langmuir I	0.45	0.015	0.13	0.935
Langmuir II	0.59	0.059	0.035	0.739
Langmuir III	0.58	0.0058	0.27	0.431
Langmuir IV	0.53	0.0066	0.24	0.431

Sorption isotherms

Analysis of equilibrium data by fitting them onto different isotherm models was done. Different dilutions i.e. 100%, 80%, 60%, 40% and 20% were made and initial hardness (C_o) was estimated. Then these different concentrations of the effluent were treated with 4g of the adsorbent in each flask. After every 20 minutes, sampling was done and hardness was estimated to calculate the equilibrium concentration (C_e). Freundlich isotherm given by Freundlich, 1906 is often used for heterogenous surface and is represented by equation:

$$q_e = K_f C_e^{1/n} \quad (1)$$

where q_e (mg/g) is the equilibrium adsorption capacity,

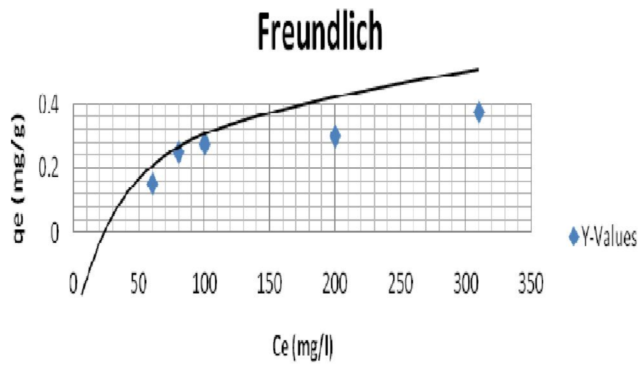

Figure 1 : Freundlich isotherm obtained using non-linear method for removal by RHAC

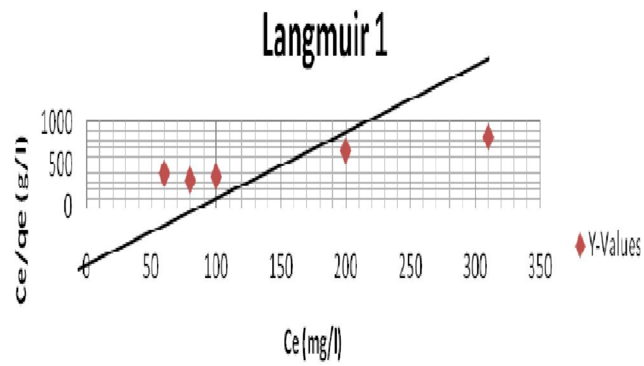

Figure 2 : Langmuir 1 adsorption isotherm using linear method for hardness removal by RHAC

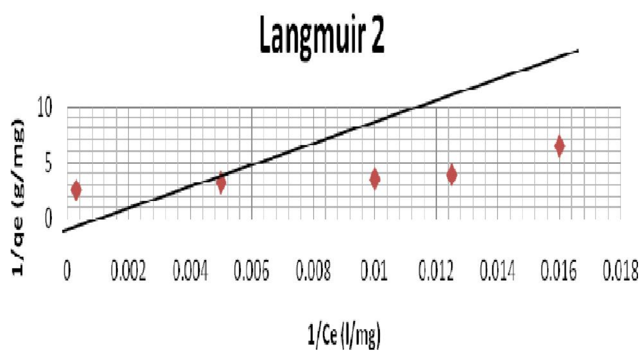

Figure 3 : Langmuir 2 adsorption isotherm using linear method for hardness removal by RHAC

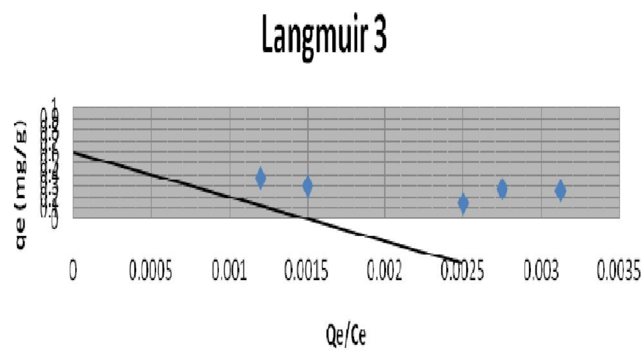

Figure 4 : Langmuir3 adsorption isotherm using linear method for hardness removal by RHAC

K_f (l/g) is Freundlich constant indicative of sorption capacity, C_e (mg/l) is the equilibrium concentration, n is the Freundlich constant indicative of sorption intensity as shown in TABLE 1 and 2.

Plot of q_e vs. C_e is parabolic in shown in figure 1. Plot of log q_e vs. log C_e is linear, whose slope is 1/n and intercept is log K_f according to the following equation:

$$\log q_e = \log K_f + 1/n (\log C_e) \quad (2)$$

which shows that the adsorption follows Freundlich isotherm. Values of Freundlich constant K_f and 1/n are calculated from plot. Plot of log q_e vs. log C_e is shown in figure 2.

Langmuir isotherm given by Langmuir, 1916 model assumes a number of factors: monolayer sorption on a set of distinct localised sorption sites; no interaction between sorbed species; all sites are energetically equivalent and adsorbent is structurally homogenous among others and is represented as:

$$q_e = q_m.K_a.C_e / 1+K_a.C_e \quad (3)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), and q_m (mg/g) and K_a (l/mg) are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively.

Linear regression is frequently used to determine the best-fitting isotherm, and the method of least squares has been used for finding the parameters of the isotherms. Langmuir isotherm can be linearized as four different types[11] (TABLE 3). Figure 2, 3, 4 and 5 shows the four linear Langmuir equations with the experimental data for hardness removal by rice husk activated carbon. The coefficient of determination, r^2, was used to test the best-fitting isotherm to the experimental data. The values of q_m, K_a and r^2 are calculated from the linear plots of Langmuir isotherm. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L)[12,13] which is defined by:

$$R_L = 1/(1 + K_a C_o) \quad (4)$$

where K_a is the Langmuir constant and C_o the highest hardness concentration (mg/l). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or

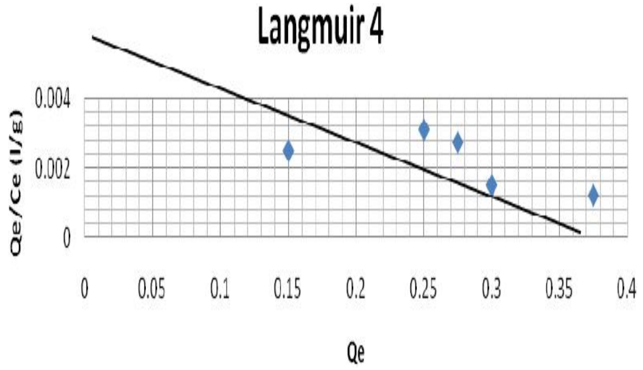

Figure 5 : Langmuir 4 adsorption isotherm using linear method for hardness removal by RHAC

irreversible ($R_L = 0$).

Experimental data was found to fit well into both, Langmuir and Freundlich adsorption isotherm equations. TABLE 3 shows the values of Langmuir constants i.e. K_a, 1/n, r^2 and R_L. The separation factor, R_L, indicates the shape of isotherm and nature of adsorption process. The R_L values for all linear forms of Langmuir isotherms come out to be in the range of $0<R_L<1$ confirming that the rice husk activated carbon is favourable for Langmuir adsorption under optimized conditions used in this research work. The value for coefficient of determination, r^2, obtained from Langmuir 1, which is close to unity (0.935), indicates that there is strong positive evidence that the removal of hardness by RHAC follows the Langmuir isotherm. If just the linear form of Langmuir-1 is used for comparison, Langmuir-1 was more suitable for the experimental data than the Freundlich Isotherm because of the higher value of the coefficient of determinations, r^2 i.e. 0.935. In contrast, if using the linear forms of the other Langmuir equations i.e Langmuir 2, Langmuir 3 and Langmuir 4, the Freundlich isotherm (r^2 0.776) was found to be more suitable for the experimental data than was the Langmuir isotherm in most cases, Langmuir 2 (r^2 0.739) Langmuir-3 (r^2 0.431) and Langmuir 4 (r^2 0.431). The maximum sorption capacity, q_m determined from linear plot of Langmuir 1, Langmuir 2, Langmuir 3 and Langmuir 4 are found to be 0.45, 0.59, 0.59 and 0.53 mg/g respectively. From the TABLE 3, it can be concluded that maximum sorption capacity, q_m is highest in case of Langmuir 2 i.e. 0.59 mg/g. From the sorption isotherm studies, it was concluded that Langmuir isotherm obtained from Langmuir 1 is more suitable for experimental data than Freundlich isotherm.

CONCLUSIONS

On optimizing all the conditions studied in this work, it was discovered that activated rice husk can compete favorably well with known commercial adsorbents. The % decolorization was found to be maximum (90-94%) at pH 2, contact time of 70-80minutes, agitation speed of 120rpm, sorbent dosage of 4g/100ml. The adsorbent could be recycled in acidic conditions and the feasibility of reuse is possible. The value of coefficient of determination, r^2, obtained from Langmuir 1, which is close to unity (0.935), indicates that there is strong positive evidence that the removal of hardness by RHAC follows the Langmuir isotherm. It can be concluded that activated rice husk can be considered a low cost alternative for treatment of waste water.

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