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Research Article

Optimization of Adsorption Conditions of Cr (VI) by PEI Modified BSG Using Response Surface Methodology

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Abstract: Surface response optimization of Adsorption Conditions of Cr (VI) wastewater by PEI modified brewer's grains (BSG) with the factors of pH value, adsorbent concentration, adsorption time, amount of adsorbent and the response of adsorption rate were studied. The optimal parameters for adsorption conditions were of adsorbent concentration of 113.30 mg/L, adsorbent particle size of 60~80 mesh, pH 1.79, adsorbent amount of 4.99 g/L, adsorption time and temperature of 1.88 h and 30°C, respectively. The maximal absorption rate got 100.0%, adsorption capacity was 46.58 mg/g. The PEI modified BSG is a promising, cheap, efficient, new biological materials of adsorption for Cr (VI) in wastewater.

Keywords: Adsorption conditions, Cr (VI), modified brewer's grains (BSG), response surface methodology

INTRODUCTION

Chromium is one of the most toxic elements (Wang *et al*., 2008). Due to its acute toxicity and the wide use in various industries, including metallurgy, leather tanning, electroplating and wood preservation, pollution by hexavalent chromium has received widespread attention. Several treatment methods use in various industries, including metallurgy, leather tanning for Cr (VI) removal from industry wastewater have been established i.e., chemical precipitation, electrolysis, activated carbon adsorption, ion exchange, reverse osmosis, etc (Prabhakaran *et al*., 2009; Vinod *et al*., 2010; Fiol *et al*., 2008; Liu and Zhang, 2011; Park *et al*., 2008). Traditional processing methods are suitable for the removal of toxic metals in high concentrations but are costly or inefficient when dealing with wastewater containing toxic metals in low concentrations. Many researchers have been actively seeking cost-effective materials to adsorb Cr(VI) ions for wastewater purification (Shen and Xu, 2010). In recent years, biosorption of employing agricultural and fermentation wastes and various kinds of microorganisms as biomass has been developed. This can remove Cr(VI) from dilute aqueous solutions and offers low-cost, abundant raw materials and an environmentally friendly process (Chen *et al*., 2010; Liu, 2012).

Brewer's grains (BSG) is the main by-product of beer industry. It is produced in large quantities yet lacks effective utilization, which results in significant environmental pollution. In this study, the waste BSG has been modified through polyethylenimine (PEI) modified and glutaraldehyde (GA) cross-linking process for preparing the modified BSG biosorbents. For utilizing the BSG as the low cost material for Cr (VI) wastewater purification and the BSG reutilization, the adsorption conditions was studied, then the results would be the theoretical basis for the comprehensive utilization of the material.

MATERIALS AND METHODS

Reagents and instruments: Preparation of PEI modified brewer's grains (BSG) biosorbent: The BSG was from the bee laboratory in our school, washed with tap water and dried at 50°C to constant weight. Then the BSG biosorbent were crushed using a universal grinder and sieved (60-80 mesh). 4 g BSG of processing were placed in 150 mL conical flask, add 100 mL of 4% PEI (polyethylene imine, molecular weight 25000) methanol solution at room temperature, shaking for 24 h. Then directly into 200 mL l.5% GA solution after the mixture, magnetic stirring for half an hour to dump the supernatant with plenty of water to clean absorbent until the supernatant clarification. The adsorbent preserved in a dryer after drying until use.

Reagents: The Cr (VI) standard solution was prepared using conventional methods and stored as 100 mg/L stock solution. The mock sewage solution was prepared by proper dilution of the stock solution. All reagents were of analytic grade. Distilled water was used throughout the experiment.

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Instruments: Electronic balance (FA1004N), 7220 spectrophotometer (Shanghai Precision Instrument Co., Ltd.), pHS-3B precision pH meter (Guangzhou Xinying Electrical Co., Ltd.), high-speed refrigerated centrifuge (GL-20G-II), HX-200 universal grinder (Hangzhou Sansi Instruments Co., Ltd.), SHA-B water bath thermostat oscillator (Shanghai Yuejin Medical Instrument Factory).

EXPERIMENTAL METHODS

Determination of Cr (VI) concentration in the mock sewa: The concentration of Cr (VI) was determined by visible spectrophotometry using 1,5-diphenylcarbohydrazide (Vinod *et al*., 2010). The absorbance A and the chromium content C (mg/L) has the following relation: A = 2.4417C+0.0007 (r = 0.9999).

Adsorption rate determination: 100 mL Cr (VI) solution were placed in 250 mL conical flask and adjusted the pH to scheduled value with 0.1 mol/L HCl or NaOH, then added the PEI modified BSG, the bottles were settled in constant warm water shaker and shaken for a scheduled time, then the grains and solution were separated by a filter, the solution were centrifuged at 5000 r/min to separated the particles and the residual Cr (VI) concentration in the filtrate was determined. Each experiment was run in three replicates. The adsorption rate (P%) were calculated by Eq. (1):

$$P\% = 100*(C_0-C_e)/C_0 \qquad (1)$$

The adsorption capacity (q) were calculated by Eq. (2):

$$q = V \times (C_0 - C_e)/W \qquad (2)$$

In which, the C_0 was the initial Cr (VI) concentration (mg/L), the C_e was the Cr (VI) concentration (mg/L) at equivalent state.V/W is the ratio of the volume of Cr (VI) solution (mL) to the amount of adsorbent (g) in a batch.

RSM optimization of adsorption conditions: Response Surface Methodology (RSM) is a method for the optimization of process parameters by analysis of isoline and a statistical method to fit he factors and response value by quadratic regression equations. RSM had been widely utilized in the field of biochemical, medical, industrial production etc (Lv *et al*., 2008; Yu *et al*., 2009; Guo *et al*., 2009). Single factors near the optimal value should be firstly found before the RSM so as to found the most approximately real situation.

100 mL of the Cr (VI) solution of 50, 100, 150, 200, 250 mg/L were shaken at 120 r/min in 250 mL conical flask, single factors experiments of different particles (20-40, 40-60, 60-80, 80-100 and over 100 meshes), PEI modified BSG quantity (2, 3, 4, 5,6 g/L), pH value (1, 2, 3, 4, 5, 6, 7), temperature (30, 40, 50, 60, 70°C), adsorption time (0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0 h) were carried out. The results showed that with the decrease of the adsorbent particles, the adsorption rate increased till the particles of 60-80 meshes, the adsorption rate reached nearly the maximal value. And the 60-80 meshes of BSG were selected in further experiments. Higher temperature is favorable to the adsorption,adsorption temperature at 70°C on adsorption of Cr (VI) is best, but Compared with 30°C, adsorption effect is difference little,considered from the economic and operational feasibility, then 30°C were selected in the following experiments. The results of other single factor experiments were listed in Fig. 1. Response surface methodology experiments of Box-Behnken design with 4 factors and 3 levels were then chosen for adsorption rate optimization of Cr(VI) adsorption by PEI modified BSG. The factors and levels were listed in Table 1.

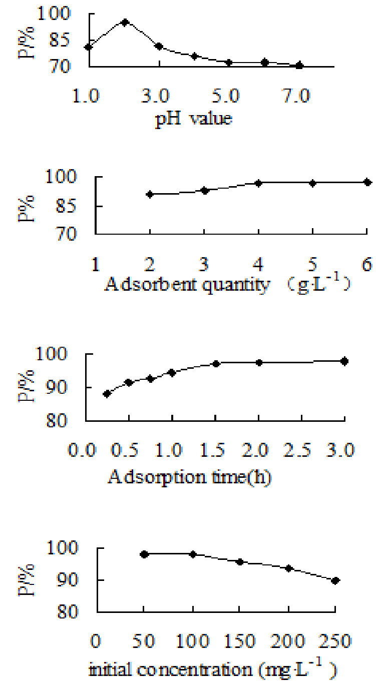

Fig. 1: Effects of different factors on Cr (VI) adsorption rate (Y-axis, %)

RESULTS AND ANALYSIS

The test results of RSM: Based on the results of single factors experiments, the adsorption rate experiments were carried out by RSM design according to Table 2.

Analysis of variance: Analysis of variance was carried out by Design expert and the results showed that the p

Table 1: Levels of factors in response surface methodology

	Levels		
Factors	-1	0	1
A pH value	1	2	3
B adsorption time (h)	0.5	1	1.5
C adsorbent quantity (g/L)	3	4	5
D initial concentration (mg/L)	100	150	200

Table 2: Data of RSM

Numbers	A	B	C	D	P/%
1	0	-1	0	-1	88.83
2	1	-1	0	0	50.47
3	0	0	0	0	92.36
4	0	-1	0	1	89.37
5	0	1	-1	0	90.14
6	-1	0	-1	0	77.05
7	1	0	0	-1	65.88
8	0	0	1	1	90.49
9	0	1	0	1	92.28
10	0	0	0	0	96.26
11	0	0	-1	-1	97.89
12	0	0	0	0	96.36
13	-1	-1	0	0	77.70
14	0	-1	-1	0	89.13
15	-1	1	0	0	82.71
16	0	0	-1	1	93.16
17	0	0	1	-1	97.76
18	1	0	1	0	56.53
19	1	1	0	0	52.33
20	0	1	1	0	97.24
21	-1	0	0	1	65.48
22	0	-1	1	0	96.16
23	0	0	0	0	97.36
24	0	0	0	0	96.56
25	1	0	-1	0	57.62
26	1	0	0	1	56.98
27	0	1	0	-1	96.40
28	-1	0	0	-1	75.66
29	-1	0	1	0	76.52

Table 3: Analyze of mean square

Source of squares	Sum of square	Degree of freedom	Mean square	F value	Prob>F
Model	7563.07	14	540.22	40.35	< 0.0001
A	1423.98	1	1423.98	106.37	< 0.0001
B	31.49	1	31.49	2.35	0.1474
C	7.86	1	7.86	0.59	0.4563
D	30.88	1	30.88	2.31	0.1511
A^2	5663.54	1	5663.54	423.07	< 0.0001
B^2	17.53	1	17.53	1.31	0.2717
C^2	1.45	1	1.45	0.11	0.7471
D^2	45.29	1	45.29	3.38	0.0872
AB	2.48	1	2.48	0.19	0.6734
AC	0.078	1	0.078	5.857E-003	0.9401
AD	69.64	1	69.64	5.20	0.0387
BC	1.225E-003	1	1.225E-003	9.151E-005	0.9925
BD	5.43	1	5.43	0.41	0.5345
CD	1.61	1	1.61	0.12	0.7337
Residual	187.42	14	13.39		
Lack of fit	172.05	10	17.20	4.48	0.0808
Pure error	15.37	4	3.84		
Cor total	7750.48	28			

values of pH value(A) was less than 0.01, which showed that the modified BSG had most important influence on Cr(VI) adsorption; the p value of the interaction of pH value (A) and initial concentration (D) was less than 0.05 and more than 0.01, which had significant influence on Cr(VI) adsorption. Analysis of variance showed that the factors and responses were not linear relationship. Above results showed that the specific factors and adsorption response did not have simple correlation relations (Table 3).

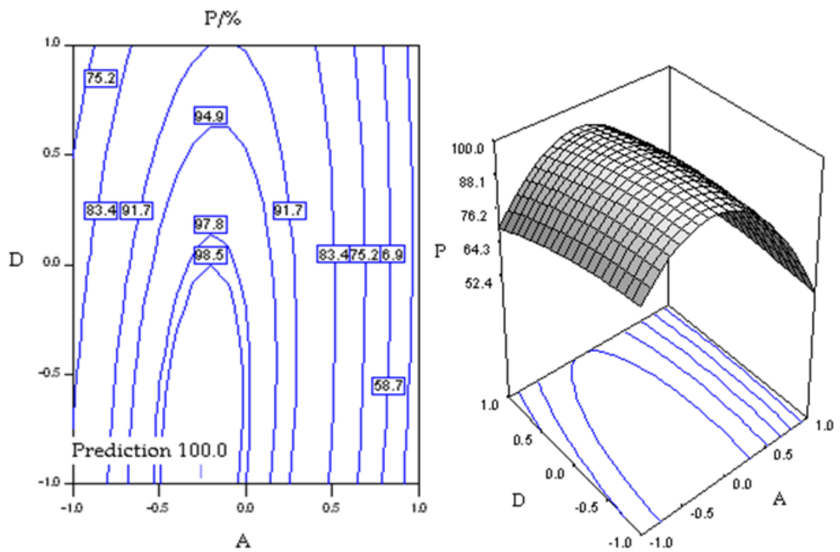

Fig. 2: The R = f (A, D) response surface and equivalent linear regression model

Table 4: Adsorption capacities of different adsorbents for Cr (VI)

Adsorbent	Maximum adsorption capacity(mg/g)	pH	Maximum initial concentration(mg/L)	Ref
Sawdust	3.3	6.0	50.0	Hamadi *et al*. (2001)
Coconut shell activated carbon	20.0	2.5		Alaerts *et al*. (1989)
Leaf mould	43.0	2.0	1000.0	Sharma and Forster (1994a)
Sawdust	39.7	2.0	1000.0	Sharma and Forster (1994a)
Maize cob	13.8	1.5	300.0	Sharma and Forster (1994b)
Sugar cane bagasse	13.4	2.0	500.0	Sharma and Forster (1994b)
Coconut husk fibers	29.0	2.1	500.0	Tan *et al*. (1993)
Palm pressed-fibers	15.0	2.0		Tan *et al*. (1993)
Chitosan cross-linked with epichlorohydrin	11.3	3.0	100.0	Qian *et al*. (2000)
PEI modified BSG	46.58	1.8	113.3	Present study

A fitting model: To fit the response surface test data, to obtain the coding variable regression equation of two order polynomial The Eq. (2):

$$P = +95.78-10.89A+1.62B+0.81C-1.60D-29.55A^2-1.64B^2+0.47C^2-2.64D^2-0.79AB-0.14AC+4.17AD+0.017BC-1.17BD-0.63CD \quad (3)$$

The p value of the model was less than 0.0001 (very significant), the lack of fit value was of 0.0808 (not significant), which showed that the model fit the RSM data significantly, the equation was of the good mathematic model fit the Cr (VI) adsorption by BSG and adsorption parameters.

Interaction analysis: In the pH value, adsorption time, adsorbent quantity, initial concentration of the four factors,any of two factors as X and Y, as the Z in the adsorption rate, make the corresponding 3D Fig. 2. The interaction between pH value (A) and initial concentration (D) had influences on the adsorption response, which showed steep curve in the figures and it is consistent with the regression analysis results.

The optimal process validation: The predicted maximal value based on the software gave the optimal adsorption conditions of: pH value 1.79, adsorption time 1.88 h, initial concentration of 113.30 mg/L, adsorbent quantity 4.99 g/L, shaker rotation of 120 r/min, under the optimal conditions, the maximal adsorption rate was of 100.0%. the verified value of the adsorption rate were of over 99% and was consistent with the predicted value, which verified the validity of the model.After the treatment of wastewater containing Cr (VI) content of less than 0.5 mg/L, meet the national wastewater discharge standard (GB8978, 1996). The adsorption capacity (q) was calculated by Eq. (2), adsorption capacity was 46.58 mg/g. Comparing adsorption capacities of different adsorbents for Cr (VI), the PEI modified BSG is a promising, cheap, efficient, new biological materials of adsorption for Cr (VI) in wastewater (Fig. 2 and Table 4).

CONCLUSION

The results of RSM showed that pH value was the most significant factor influencing the adsorption performance of PEI modified BSG. The optimal processing conditions were as follows: adsorbent concentration of 113.30 mg/L, adsorbent particle size of 60~80 mesh, pH 1.79, adsorption time and temperature of 1.88 h and 30°C, respectively, adsorbent amount of 4.99 g/L. The maximal adsorption rate was of 100.0%, adsorption capacity was 46.58 mg/g.

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