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Research Article

Optimization of Adsorption Conditions of Cr(VI) by Amine Surfactant Modified Brewer's Grains in Food Industry using Orthogonal Test

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Abstract: Orthogonal experiment optimization of adsorption conditions with the factors of pH value, adsorption time, adsorbent amount of Cr(VI) wastewater by amine surfactant Modified Brewer's Grains (MBSG) in food industry were studied. The results showed that optimum adsorption conditions were as follows: 100 mL Cr(VI) ions solution of 250 mg/L, adding 2.0 g/L brewer's grains of 60~80 mesh and adsorbed for 1.0 h, adsorbent temperature 30°C, pH 3.0. Under the optimal conditions, the maximal absorption rate got 90.18% and adsorption capacity was 111.95 mg/g. The modified MBSG is a promising, cheap, efficient, new biological materials of adsorption for Cr(VI) in wastewater.

Keywords: Adsorption conditions, Cr(VI), Modified Brewer's Grains (MBSG), orthogonal experiment

INTRODUCTION

Chromium is one of the most toxic elements and is widely present in the form of chromium (VI) in wastewater (Wang *et al*., 2008). The potential sources of chromium (VI) wastes are effluents from metallurgy, electroplating, leather tanning, textile dyeing, paint, ink and aluminium manufacturing industries (Liu, 2012; Liu and Zhang, 2011). The conventional methods for treatment of chromium (VI) wastes include: chemical precipitation, electrolysis, activated carbon adsorption, reverse osmosis, ion exchange, etc (Liu, 2012). These techniques have limitations, often are neither effective nor economical especially for the removal of heavy metals at low concentrations and often generate chemical sludge, whose disposal is problematic. Many researchers have been actively seeking cost-effective materials to adsorb Cr(VI) ions for wastewater purification (Shen and Xu, 2010). Biological adsorption method had been concerned for the advantages of low cost, simple operation and non-secondary pollution, etc. Numerous reports have been made on the removal of Cr(VI) from aqueous solutions using different organisms as adsorbents, including bacteria, algae, fungi, seaweed, agricultural biowastes and industrial byproducts (Chen, 2009). The mechanism for Cr(VI) biosorption is usually based on adsorption-coupled reduction and electron transfer in the process of reduction and adsorption as well as the sorption sites involved in the redox reaction between Cr(VI) and biomass have been investigated (Park *et al*., 2007; Li *et al*., 2010). Various reports have showed that the functional groups involved in the adsorption-coupled reduction reaction depend on the type of biomass; and amino, carboxyl, sulfonate, thiol, phenolic and lignin, tannin groups of biomaterials have been reported as Cr(VI) sorption sites or electron-donor groups (Deng and Ting, 2005; Yang and Paul Chen, 2008).

Brewer's Grains (BSG) is the main by-product of beer industry. It is produced in large quantities yet lacks effective utilization. It have good hydrophilicity and easily adsorbed porous structure, containing a large number of hydroxyl groups. The metal ion adsorption ability was increased by chemical modification of active groups (Cui *et al*., 2011; Chen, 2009). In this study, the waste BSG has been modified by amine reaction with brewer's grains that using N, N-Dimethyl formamide (DMF) as dissolvent, epichlorohydrin (ECH) as etherfying agent, triethylenete tramine (TETA) as cross-linking agent and introduce amino group for preparing the modified BSG biosorbents (MBSG). For utilizing the BSG as the low cost material for Cr(VI) wastewater purification, the adsorption conditions was studied using orthogonal test of the adsorption rate and adsorption amount as index, then the results would be the theoretical basis for the comprehensive utilization of the material.

MATERIALS AND METHODS

Reagents and instruments:

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Reagents: All reagents were of analytic grade. Distilled water was used throughout the experiment. 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.

Instruments: 7220 spectrophotometer (Shanghai Precision Instrument Co., Ltd.), electronic balance (FA1004N), pHS-3B precision pH meter (Guangzhou Xinying Electrical Co., Ltd.), SHA-B water bath thermostat oscillator (Shanghai Yuejin Medical Instrument Factory).

Experimental methods:

Preparation of absorbent: The initial 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) and the resulting particles were stored in a desiccator until use.

Adsorbent modification method: 4 g brewer's grains of processing were placed in 100 mL three round bottom flask, add 15 mL ECH and 15 mL DMF at 85°C water bath stirring 1 h. Then added dropwise to 4 mL TETA, mixing reaction 1 h at 85°C. Remove the sample from the three round bottom flask washing with distilled water, dried with filtering machine and then placed in 105°C oven drying 5 h. Then the brewer's grains biosorbent were crushed using a universal grinder and sieved (60-80 mesh) and the resulting particles were stored in a desiccator until use.

Adsorption experiment: 100 mL 250 mg/L Cr(VI) solution were placed in 250 mL conical flask and adjusted the pH to 2.0, then added the MBSG of 2.0 g/L, the bottles were settled in constant warm water shaker of 30°C and shaken for 2 h, 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 concentration of Cr(VI) was determined by visible spectrophotometry using 1,5-diphenylcarbohydrazide (Singh *et al*., 2005). The absorbance *A* and the chromium content *C* (mg/L) has the following relation:

$A = 2.4417C + 0.0007$ (r = 0.9999).

The adsorption rate (P%) were calculated by the following equation:

$$p = (1 - C_0 / C_e) \times 100\% \tag{1}$$

The adsorption capacity (q) was calculated with the following formula:

$$q = V \times (C_0 - C_e) / W \tag{2}$$

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

Orthogonal experiment optimization of adsorption conditions: With less test times, high efficiency, simple calculation and other advantages, the orthogonal test design has been widely applied in many research fields of medical, industrial production etc (Taguchi, 1987; Ma *et al*., 2000). Adsorption experiment optimization including pH value, adsorption time, adsorbent quantity, adsorption temperature, initial concentration choice, for which several factors are parallel single factor experiment, study their influence on adsorption. Single factors near the optimal value should be firstly found before the orthogonal test so as to found the most approximately real situation.

100 mL of the Cr(VI) solution of 100, 150, 200, 250, 300 mg/L, respectively 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), temperature (20,25, 30, 35, 40°C), pH value (1, 2, 3, 4, 5, 6, 7,8), adsorbent quantity (1, 2, 3, 4, 5, 6 g/L), adsorption time (0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0 h) were carried out. The single factor test results in addition to the adsorbent emperature and adsorbent particles were shown in Fig. 1.

The results showed that with the increasing of adsorbent temperature from 20 to 40°C, the adsorption rate and the biosorption capacity increase with increase in the adsorbent temperature. At higher temperatures the energy of system seemed to facilitate the Cr(VI) attachments onto biosorbent surfaces. Higher temperature is favorable to the adsorption. Hence, the adsorption was an endothermic process. Adsorption temperature at 40°C on adsorption of Cr(VI) is best, but compared with 30°C, adsorption effect is changed little, considered from the economic and operational feasibility, then 30°C were selected in the following experiments.

With the decrease of the adsorbent particles, the adsorption effects increased till the particles of 60-80 meshes, the adsorption effects reached nearly the maximal value. And the 60-80 meshes of MBSG were selected in further experiments.

The solution pH is the most important parameter in heavy metal biosorption. The speciation of metals in the solution is pH dependent (Dai *et al*., 2012). At the same time, the state of chemically active sites is changed by the solution pH. The solution pH was varied in the range from 1-9, by using 0.1 mol/L sulfuric acid and 0.1 mol/L sodium hydroxide conditioning agent. As shown in Fig. 1, maximum removal of Cr(VI) was achieved at pH 1. The adsorption efficiency was not significantly different at pH<5. These groups are

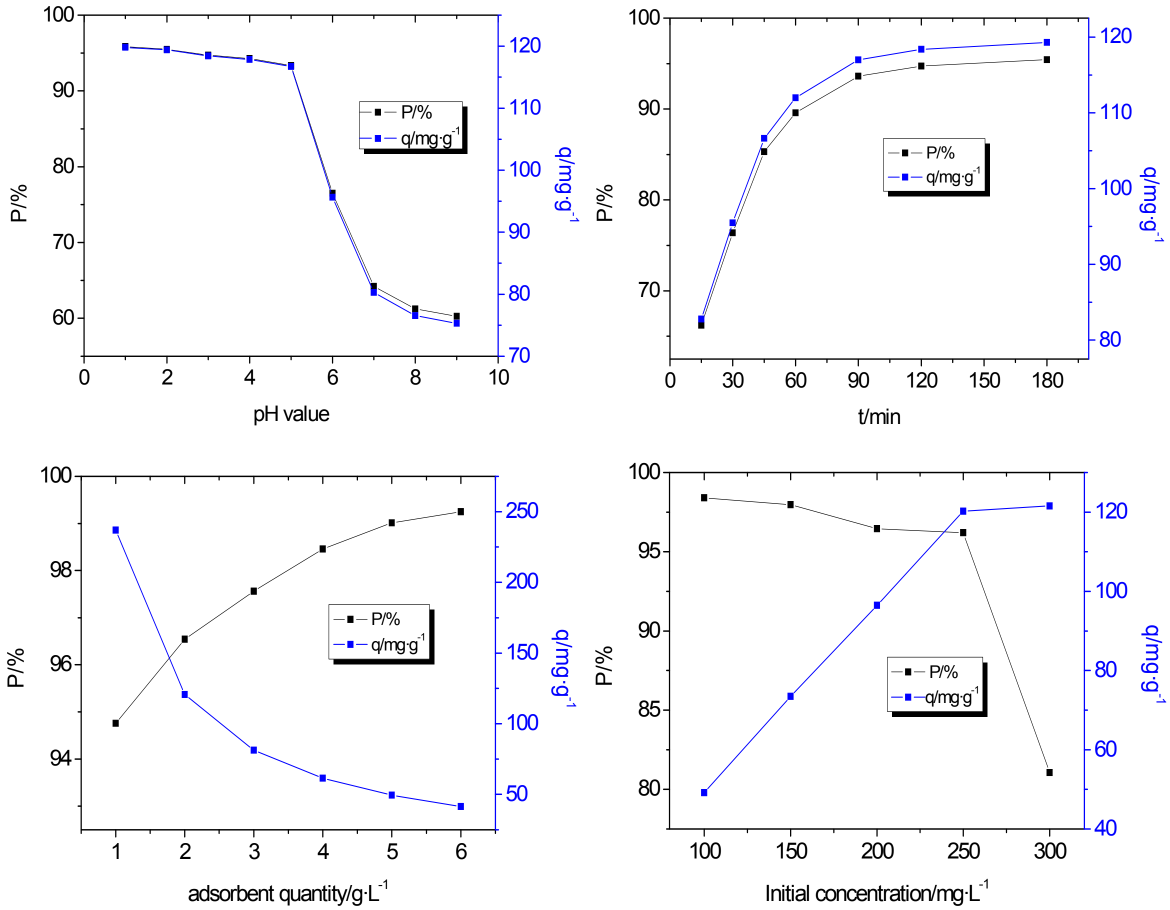

Fig. 1: Effects of different factors on Cr(VI) adsorption rate

Table 1: Levels and factors of orthogonal experiment design

Level	A pH value	B adsorption time /h	C adsorbent quantity/g/L	D initial concentration /mg/L
1	3	1	1	200
2	4	2	2	250
3	5	3	3	300

negatively charged at higher pH and are positively charged when protonated at low pH. The dominant form of Cr(VI) is $HCrO^-_4$ (Huang *et al*., 2013; Shen and Xu, 2010) at low pH which was attracted by positively charged sites. Because the general electroplating chromium containing wastewater, the pH value was 3.5~6.5. So three level of pH is set to 3, 4, 5.

Figure 1, the adsorption rate and the biosorption capacity increase with increase in the adsorbent time, adsorption rate is already above 90% when the adsorption time is 1 h. So three level of adsorption time is set to 1, 2, 3 h.

The removal efficiency and specific uptake of metals depend on type and quantity of the biosorbent. If no information is available, for particular type of biomass it is better to find the optimal dose, experimentally. As revealed in Fig. 1, the biosorption capacity decreased with increase and the adsorption rate increased with increase in biosorbent dose. There was negligible increase in the adsorption rate beyond the dose of 2 g/L. Considering these results, a dose of 2 g/L was considered sufficient, for the optimal removal of Cr(VI). Moreover, the biosorption capacity was high at low dose rates. This may be the availability of lesser binding sites and these were fully utilized.

The effects of initial Cr(VI) concentration on the MBSG adsorption have been investigated by varying the initial Cr(VI) concentration from 100 to 300 mg/L as shown in Fig. 1. It is found that the biosorption capacity increase and the adsorption rate decreases with increase in the Cr (VI) concentration. Considering the adsorption capacity and adsorption rate, initial Cr(VI) concentration of 250 mg/L was for the optimal removal of Cr(VI).

According to Fig. 1, we designed the L_9 (3^4) program of orthogonal test, the factors and levels were listed in Table 1. Results were disposed by the intuitive analysis and variance analysis, significant test of Cr(VI) adsorption factor by Duncan (Du,1999).

RESULTS AND ANALYSIS

The test results of orthogonal experiment: Based on the results of single factors experiments, the adsorption

Table 2: Orthogonal experimental program and results of adsorption (n = 3)

No.	A	B	C	D	P/%	q/mg/g
1	1	1	1	1	P/%	q/mg/g
2	1	2	2	2	65.30	130.59
3	1	3	3	3	90.94	113.67
4	2	1	2	3	96..00	96.00
5	2	2	3	1	71.84	107.76
6	2	3	1	2	98.13	65.42
7	3	1	3	2	53.36	133.40
8	3	2	1	3	96.48	80.40
9	3	3	2	1	43.68	131.05
K_1	84.08	77.87	54.11	81.27	P/%	
K_2	74.44	77.58	81.05	80.26		
K_3	73.51	76.58	96.87	70.51		
R	10.57	1.30	42.76	10.76		
K_1	113.42	106.25	131.68	95.46	q/mg/g	
K_2	102.19	103.38	103.93	109.16		
K_3	100.61	106.59	80.61	111.60		
R	12.81	3.21	51.07	16.14		

experiments were carried out by orthogonal experiment design according to Table 2.

The intuitive analysis: From Table 2 can be seen, the effect of the adsorbent quantity on the rate of adsorption and the adsorption capacity were the maximum. The range of data R was visible, the effect order of various factors on the rate of adsorption: adsorbent quantity > initial concentration > pH value > adsorption time, the optimum adsorption conditions were: $A_1B_1C_3D_1$. The effect order of various factors on the adsorption capacity is the same to the adsorption capacity, the optimum adsorption conditions were: $A_1B_3C_1D_3$. The result of orthogonal experiment is consistent with the single factor experiment mainly.

The analysis of variance: We can see from Table 3, the adsorbent quantity was a highly significant influencing factor on the rate of adsorption and the adsorption capacity. The initial concentration and pH value were significant influencing factors on the rate of adsorption and the initial concentration was significant influencing factor on the adsorption capacity. The adsorption time is not significant factor. It could consider to determine, as determined by the Duncan method after checking back.

The duncan analysis: First were found between the level of various factors $r_{0.05,}$ $r_{0.05}$ ($r_{0.05}$ = 6.09, $r_{0.01}$ = 14), then calculate the value of R_k (standard error were 1.354, 1.421 on the rate of adsorption and the adsorption capacity, respectively, the R_k = standard error *r). According to the calculation results, it was compared for each factor level significantly. From Table 4 can be seen, adsorbent quantity had significant differences each other on the rate of adsorption and the adsorption capacity. The pH value of 3.0 was significantly to the other. The initial concentration of 300 mg/L was significantly to the other on the rate of adsorption and the initial concentration of 200 mg/L was significantly to the other on the adsorption

Table 3: Analysis of variance

	Source of variation	SS	df	MS	F	Significance
P/%	A	205.4614	2	102.7307	73.9383	*
	B	2.7788	2	1.3894	1.0000	
	C	2803.989	2	1401.9945	1009.0566	**
	D	211.9185	2	105.9592	76.262	*
	SS_T	3224.1476	8			
q/mg/g	A	292.7371	2	146.3685	15.6908	
	B	18.6566	2	9.3283	1.0000	
	C	3922.4963	2	1961.2481	210.2471	**
	D	454.1921	2	227.0960	24.3448	*
	SS_T	4688.0820	8			

$F_{0.01}(2, 2)$ = 99.00, $F_{0.05}(2, 2)$ = 19.00, "*" Represents a significant influencing factors, "**" Represents a highly significant influencing factors

Table 4: Compare significant difference in four levels of factors

1(A)				2(B)				
Level	P	$P_{0.05}$	$P_{0.01}$	Level	P	$P_{0.05}$	$P_{0.01}$	
1	84.08	a	A	1	77.87	a	A	P/% q/mg/g
2	74.44	b	A	2	77.58	a	A	
3	73.51	b	A	3	76.58	a	A	
1	113.42	a	A	3	106.59	a	A	
2	102.19	b	A	1	106.25	a	A	
3	100.61	b	A	2	103.38	a	A	
3(C)				4 (D)				
Level	P	$P_{0.05}$	$P_{0.01}$	Level	P	$P_{0.05}$	$P_{0.01}$	
3	96.87	a	A	1	81.27	a	A	P/% q/mg/g
2	81.05	b	B	2	80.26	a	A	
1	54.11	c	C	3	70.51	b	A	
1	131.68	a	A	3	111.60	a	A	
2	103.93	b	B	2	109.16	a	A	
3	80.61	c	C	1	95.46	b	A	

Table 5: Adsorption capacities of different adsorbents for Cr(VI)

Adsorbent	Maximum capacity (mg/g)	Adsorption pH	Ref
Coconut husk fibers	29.0	2.1	Tan *et al*. (1997)
Leaf mould	43.0	2.0	Sharma and Forster (1994a)
Maize cob	13.8	1.5	Sharma and Forster (1994b)
Rice husk carbon	48.31	2.0	Bansal *et al*. (2009)
Sawdust	39.7	2.0	Sharma and Forster (1994b)
Sawdust (carbonized)	53.48	2.0	Bansal *et al*. (2009)
Sugar cane bagasse	13.4	2.0	Sharma and Forster (1994b)
Tamarindus indica seeds	98.04	2.0	Agarwal *et al*. (2006)
Walnut hull	98.13	1.0	Wang and Chen (2009)
MBSG	111.95	2.0	Present study

capacity. Considering the use of energy and resources, comprehensive analysis to determine the optimal adsorption conditions of Cr(VI) was $A_1B_1C_2D_2$.

The optimal process validation: Under the optimal adsorption conditions, repeated for 3 times, the adsorption rate were: 90.09, 90.19, 90.26%, respectively the average of adsorption rate was 90.18%, RSD = 1.84%. The adsorption capacity were: 111.23, 112.02, 112.61 mg/g, respectively the average of adsorption rate was 111.95 mg/g, RSD = 1.48%. It was the same basically to result of orthogonal experiment. Comparing adsorption capacities of different adsorbents for Cr(VI), the MBSG is a promising, cheap, efficient, new biological materials of adsorption for Cr(VI) in wastewater (Table 5).

CONCLUSION

The results of orthogonal experiment showed that the adsorbent quantity was a highly significant influencing factor on Cr(VI) adsorption rate and adsorption capacity. The optimal processing conditions were as follows: pH value 3.0, adsorption time 1.0 h, initial concentration of 250 mg/L, adsorbent quantity 2.0 g/L, adsorbent temperature 30 °C, shaker rotation of 150 r/min, the particles of 60-80 meshes. Under the optimal conditions, the average of adsorption rate was 90.18% and adsorption capacity was 111.95 mg/g. The modified MBSG is a promising, cheap, efficient, new biological materials of adsorption for Cr(VI) in wastewater.

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