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Research Article

Synthesis Technology of PEI Modified Brewer's Grains for the Adsorption of Cr(VI)

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Abstract: With beer production waste brewer's grains (BSG) as the raw material, through polyethylenimine (PEI) modified and glutaraldehyde (GA) cross-linking process for preparing the modified brewer's grains biosorbents. The simulation of Cr (VI) wastewater as treatment object, through the optimization of synthesis conditions of Cr (VI), the optimal synthesis process was obtained. The results showed, 4 g BSG and 100 mL 4% PEI methanol solution were placed in 250 mL conical flask at room temperature, shaking for 24 h. After the mixture,shifted to 200 mL 1.5% GA solution directly, magnetic stirring for half an hour, the modified results of brewer's grain was best. Under the optimal conditions, the average of adsorption rate was 98.82% and adsorption capacity was 45.31 mg/g. The modified brewer's grains of amine surfactant modified is a promising treatment of chromium wastewater biological materials.

Keywords: Cr(VI), Modified BSG, orthogonal experiment, PEI, synthesis conditions

INTRODUCTION

Chromium is one of the most toxic elements (Wang *et al*., 2008) and is the wide use in various industries, including metallurgy, leather tanning, electroplating and wood preservation, pollution by hexavalent chromium has received widespread attention. Traditional processing methods (e.g., chemical precipitation, electrolysis, activated carbon adsorption, ion exchange, reverse osmosis, etc.) (Liu and Zhang, 2011) 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. Biological adsorption method had been concerned for the advantages of simple operation, low cost and non-secondary pollution, etc (Shen and Xu, 2010; Sud *et al*., 2008; Park *et al*., 2008). Numerous reports have been made on the removal of Cr(VI) from aqueous solutions using different organisms as adsorbents, including bacteria, algae, fungi, seaweed, industrial byproducts and agricultural biowastes (Mohan and Jr. Pittman, 2006). 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, phenolic, sulfonate, thiol and lignin, tannin groups of biomaterials have been reported as Cr(VI) sorption sites or electron-donor groups (Elangovan *et al*., 2008; Ertugay and Bayhan, 2008; Li *et al*., 2008; Nakano *et al*., 2001; Park *et al*., 2005; Deng and Ting, 2005; Yang and 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 (Chen, 2009). In this study, the waste BSG has been modified through polyethylene imine (PEI) modified and glutaraldehyde (GA) cross-linking process to generate suitable bio-sorption material, so as to utilize the BSG as the low cost material for Cr(VI) wastewater purification, then the results would be the theoretical basis for the comprehensive utilization of the BSG.

MATERIALS AND METHODS

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

Adsorbent modification method: 4 g BSG of processing were placed in 150 mL conical flask, add 100 mL of certain concentration of PEI (polyethylene

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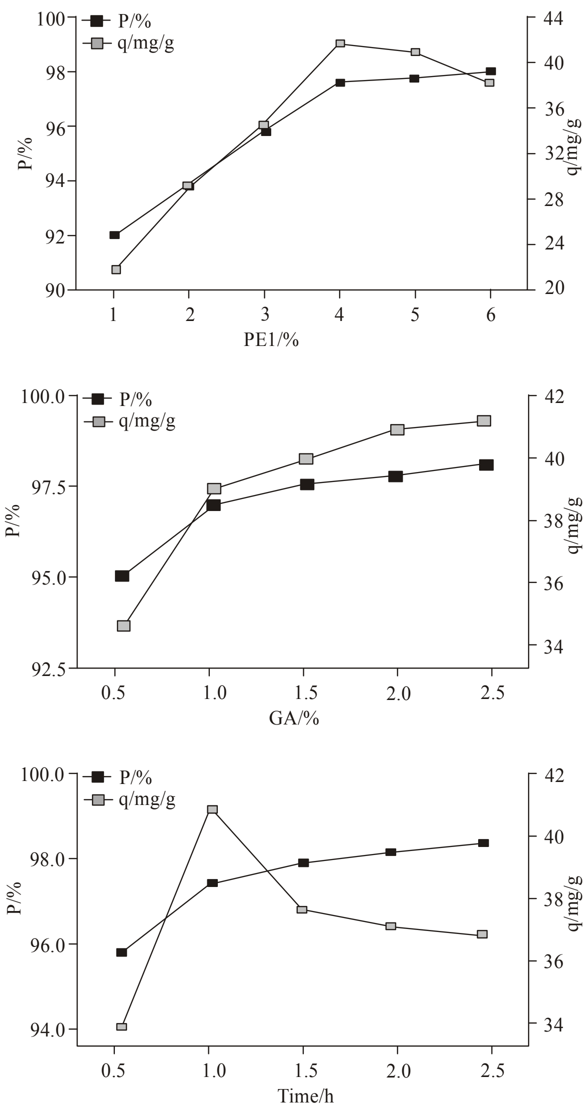

Fig. 1: Effects of different factors on Cr(VI) adsorption rate and adsorption capacity

imine, molecular weight 25000) methanol solution at room temperature, shaking for 24 h. Then directly into 200 mL of certain concentration GA solution after the mixture, magnetic stirring after a certain time to dump the supernatant with plenty of water to clean absorbent until the supernatant clarification. The adsorbent preserved in a dryer after drying (Liu, 2012).

Adsorption experiment: 100 mL 200 mg/L Cr(VI) solution were placed in 250 mL conical flask and adjusted the pH to 2.0, then added the modified BSG of 4.0 g/L, the bottles were settled in constant warm water shaker of 30ºC 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

Table 1: Levels and factors of orthogonal experiment design

Level	A PEI/%	B GA/%	C time/h
1	2	0.5	0.5
2	4	1.0	1.0
3	6	1.5	1.5

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:

$$p = (1 - C_0 / C_e) \times 100\% \quad (1)$$

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

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

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.

Orthogonal experiment optimization of synthesis conditions: The orthogonal test design has been widely applied in many research fields of medical, industrial production etc with less test times, high efficiency, simple calculation and other advantages (Guo *et al*., 2011; Elmas *et al*., 2013). Synthesis experiment optimization including cross-linking time,PEI concentration, GA concentration choice, for which several factors are parallel single factor experiment, study their influence on synthesis. The single factor test results were shown in Fig. 1. According to Fig. 1, we designed the $L_9(3^3)$ program of orthogonal test in Table 1. Results were disposed by the intuitive analysis and variance analysis, significant test of Cr(VI) adsorption factor by Duncan (Qian, 1999).

RRESULTS AND ANALYSIS

The test results of orthogonal experiment: Based on the results of single factors experiments, the adsorption 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 PEI dosage 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: PEI dosage>GA dosage>cross-linking time, the optimum synthesis conditions were:

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	91.33	24.27
2	1	2	2	2	94.23	34.85
3	1	3	3	3	95.98	31.12
4	2	1	2	3	97.26	43.45
5	2	2	3	1	97.35	47.47
6	2	3	1	2	98.21	39.44
7	3	1	3	2	96.84	35.37
8	3	2	1	3	96.32	37.26
9	3	3	2	1	98.47	46.69
K_1	93.85	95.14	95.29	95.72	P/%	
K_2	97.61	95.97	96.65	96.43		
K_3	97.21	97.55	96.72	96.52		
R	3.760	2.410	1.440	0.800		
K_1	30.08	34.36	33.66	39.48	q/mg/g	
K_2	43.45	39.86	41.66	36.55		
K_3	39.77	39.08	37.99	37.28		
R	13.37	5.500	8.010	2.920		

Table 3: Analysis of variance

	Source of variation	SS	df	MS	F	Significance
P/%	A	23.05810	2	11.52900	23.7892	*
	B	6.561300	2	3.280600	6.76930	
	C	6.027800	2	3.013900	6.21890	
	D	0.969300	2	0.484600	1.00000	
	SS_T	36.61640	8			
q/mg/g	A	286.3492	2	143.1746	20.5872	*
	B	53.09500	2	26.54750	3.81730	
	C	96.37350	2	48.18670	6.92880	
	D	13.90910	2	6.954500	1.00000	
	SS_T	449.7267	8			

$F_{0.05}(2, 2) = 19.00$; "*"represents a 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	$P_{0.05}$	$P_{0.01}$	
2	97.71	a	A	3	97.65	a	A	P/% q/mg/g
3	97.21	a	A	2	95.97	b	A	
1	93.85	b	A	1	95.14	b	A	
2	43.45	a	A	2	39.86	a	A	
3	39.77	b	A	3	39.08	a	A	
1	30.08	c	B	1	34.36	b	A	
3(C)				4(D)				
Level	P	$P_{0.05}$	$P_{0.01}$	Level	P	$P_{0.05}$	$P_{0.01}$	
3	96.72	a	A	2	96.53	a	A	P/% q/mg/g
2	96.65	a	A	3	96.52	a	A	
1	95.39	a	A	1	95.72	a	A	
2	41.66	a	A	1	39.48	a	A	
3	37.99	b	A	3	37.28	a	A	
1	33.66	c	A	2	36.55	a	A	

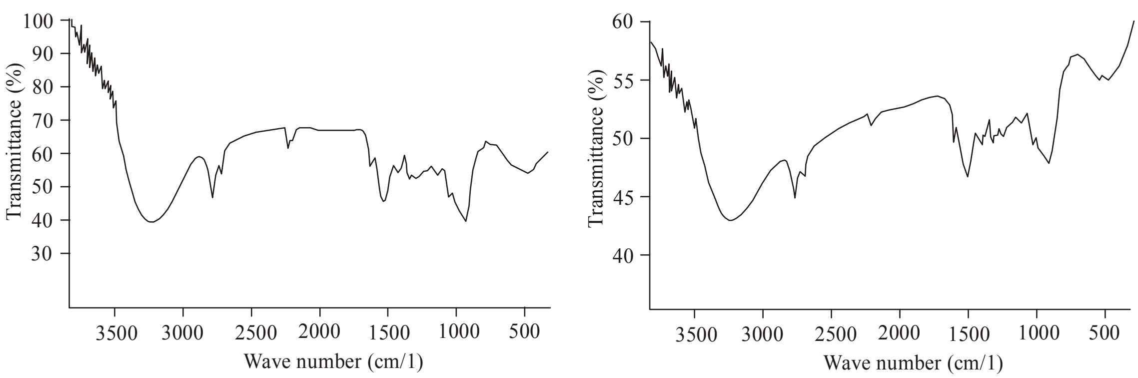

Fig. 2: Infrared spectra of BSG (upper: before modified; upper: after modified)

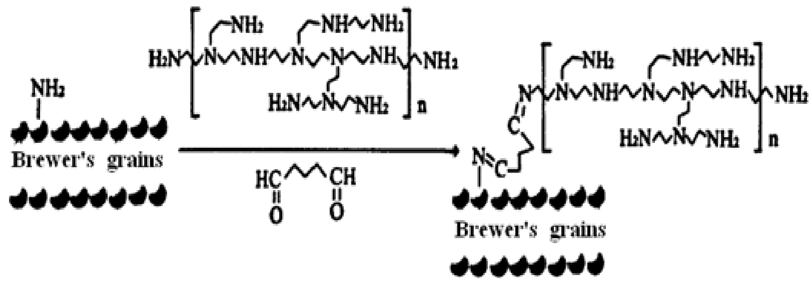

Fig. 3: Schematic depiction of the grafting process of PEI on the BSG

$A_2B_3C_3$. The effect order of various factors on the adsorption capacity: PEI dosage>cross-linking time> GA dosage, the optimum synthesis conditions were: $A_2B_2C_2$. The result of orthogonal experiment is consistent with the single factor experiment mainly.

The analysis of variance: We can see from Table 3, the PEI dosage was significant influencing factor on the rate of adsorption and the adsorption capacity. The other factor 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 0.354, 0.602 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, PEI dosage and cross-linking time had significant differences each other on the adsorption capacity. The GA dosage of 1.5% was significantly to the other. Considering the use of energy and resources, comprehensive analysis to determine the optimal synthesis conditions of Cr(VI) was $A_2B_3C_2$.

The optimal process validation: Under the optimal synthesis conditions, repeated for 3 times,the adsorption rate were: 98.85, 98.80 and 98.82%, respectively, the average of adsorption rate was 98.82%, RSD = 1.68%. The adsorption capacity were: 45.23, 45.30, 45.41 mg/g, the average of adsorption rate was 45.31 mg/g, RSD = 3.67%. It was the same basically to result of orthogonal experiment.

FT-IR Spectra: For a qualitative and preliminary analysis of the main functional groups that can be involved in modifying, FT-IR analysis of the solid phase was performed using a Fourier Transform Infrared spectrometer (FT-IR, Thermo Scientific Nicolet is10). FT-IR spectra of the BSG materials before and after modified. For the FT-IR study, approximately 2 mg of finely ground BSG materials was encapsulated in 200 mg of KBr to make translucent sample disks. Samples were scanned 15 times between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1}. The infrared spectra of the BSG and the PEI-modified BSG materials are shown in Fig. 2.

The infrared spectrum showed that almost all the wave strength were increased and all the wave peaks changed little after modifying, such as the stretching vibration of N-H at 3300-3500 cm^{-1}, bending vibration of N-H at 1641 cm^{-1}, stretching vibration of C-N at 1420-1460 cm^{-1}. Almost no significant changes of the functional group were visible after PEI modification. Because the nitrogen functional groups containing grains is single, only have NH_2 (NH) (Deng *et al*., 2008; Li *et al*., 2009), PEI modified by the introduction of NH_2 (NH) (Liu, 2012). Schematic depiction of the grafting process of PEI on the BSG is shown in Fig. 3. Compare the change of modified with infrared spectra, the effect is not significant.

CONCLUSION

The results of orthogonal experiment showed that the PEI dosage was significant influencing factor on Cr(VI) adsorption rate and adsorption capacity. The optimal processing conditions were as follows: PEI dosage was 4 mL, GA dosage was 1.5 mL, cross-linking time was 1 h. Under the optimal conditions, the average of adsorption rate was 98.82% and adsorption capacity was 45.31 mg/g. The modified BSG is a promising, cheap, efficient, new biological materials of adsorption for Cr(VI) in wastewater.

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