

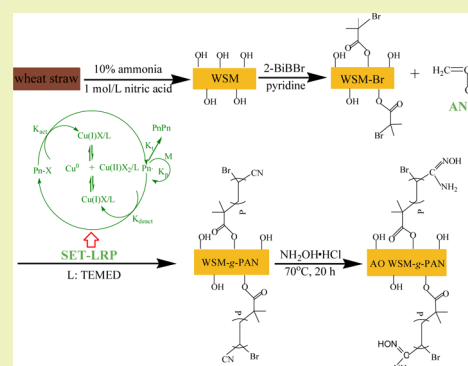
# Preparation of Wheat Straw Matrix-*g*-Polyacrylonitrile-Based Adsorbent by SET-LRP and Its Applications for Heavy Metal Ion Removal

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**ABSTRACT:** Polyacrylonitrile (PAN) was grafted onto the surface of a wheat straw matrix (WSM) by single-electron transfer-living radical polymerization (SET-LRP). A novel agricultural residue adsorbent amidoxime WSM-*g*-PAN (AO WSM-*g*-PAN) was obtained by modifying WSM-*g*-PAN with hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl). AO WSM-*g*-PAN was used to remove heavy metal ions. Compared with WSM, the adsorption capacity of AO WSM-*g*-PAN for Hg(II) increased greatly, and the maximum adsorption capacity was 4.7 mmol g<sup>-1</sup>. AO WSM-*g*-PAN could effectively adsorb Hg(II) from binary ion systems in the existence of Ni(II), Pb(II), Cu(II), Zn(II), and Ag(I).

**KEYWORDS:** *Wheat straw, Adsorbent, SET-LRP, Adsorption, Hg(II)*



## INTRODUCTION

Pollution of heavy metal ions is considered a serious environmental issue because it is a major contributor to water contamination. These substances characterized by high toxicity and carcinogenic properties limit the utilization of surface water and groundwater in many aspects.<sup>1</sup> Moreover, continuous exposure to metal ions such as Hg(II) has a seriously toxic effect on the central nervous system and living organisms.<sup>2</sup> Adsorption technology is the most commonly used method dealing with heavy metal ion pollution owing to its high efficiency.<sup>3,4</sup> However, the large capital and high regeneration costs of adsorbent increase the price of wastewater treatment.<sup>1</sup> Great efforts have been directed to explore relatively cheap materials for production of low-cost adsorbents in recent years. Agricultural residues represent one of the most promising materials in adsorbents with their unique low-cost accessibility, biodegradability and natural adsorption property. A variety of agricultural residues including rice husks,<sup>5,6</sup> maize leaf,<sup>7</sup> peanut hull pellets,<sup>8</sup> grape stalk wastes,<sup>9</sup> and wheat straw<sup>10,11</sup> have been investigated in adsorption processes. Liu et al. prepared a novel wheat straw cellulose-*g*-polypotassium acrylate/poly(vinyl alcohol) (WSC-*g*-PKA/PVA) superabsorbent utilizing conventional free radical polymerization that formed free radical sites on the cellulose backbone by chemical methods.<sup>10</sup> In the polymerization process, the polymeric chains were grafted from the free radical sites, which resulted in chain degradation of cellulose during the formation grafting sites, different grafted chain lengths, and low control over the polymerization process, especially large amounts of homopolymer formation.<sup>12</sup>

Reversible deactivated radical polymerization (RDRP) cannot only avoid the above drawbacks but also provide a possibility to tailor the surface properties of cellulose. Single-electron transfer-living radical polymerization (SET-LRP) has already been proven as a facile and versatile strategy for RDRP, which was first reported by Percec and co-workers.<sup>13–16</sup> Unlike the normal atom transfer radical polymerization process, SET-LRP undergoes an outer-sphere single-electron transfer process that has very low activation energy, which makes it possible to polymerize low active monomer acrylonitrile.<sup>17</sup> Moreover, the low concentration of growing radicals during equilibrium ensured a steady growth of polymer chains and avoided formation of a homopolymer. SET-LRP also has demonstrated its potential in the grafting polymerization from cellulose<sup>18,19</sup> and hemicellulose<sup>20</sup> and attracted significant interests due to the rapid synthesis of well-defined polymers such as functionalized acrylates<sup>21–23</sup> and vinyl chloride.<sup>24</sup>

Research on functionalized adsorbents prepared from agricultural residue has been reported in the past, but there is little information concerning the amidoxime-functionalized wheat straw adsorbent synthesized by SET-LRP and used for Hg(II) removal. Wheat straw is one of the best-known fiber crop residues and exhibits its potential in adsorbing heavy metal ions. Moreover, the existence of a large amount of available hydroxyl groups in cellulose was favorable for actuating a series of chemical reactions, such as esterification and copolymerization. So in the present study, a novel adsorbent amidoxime

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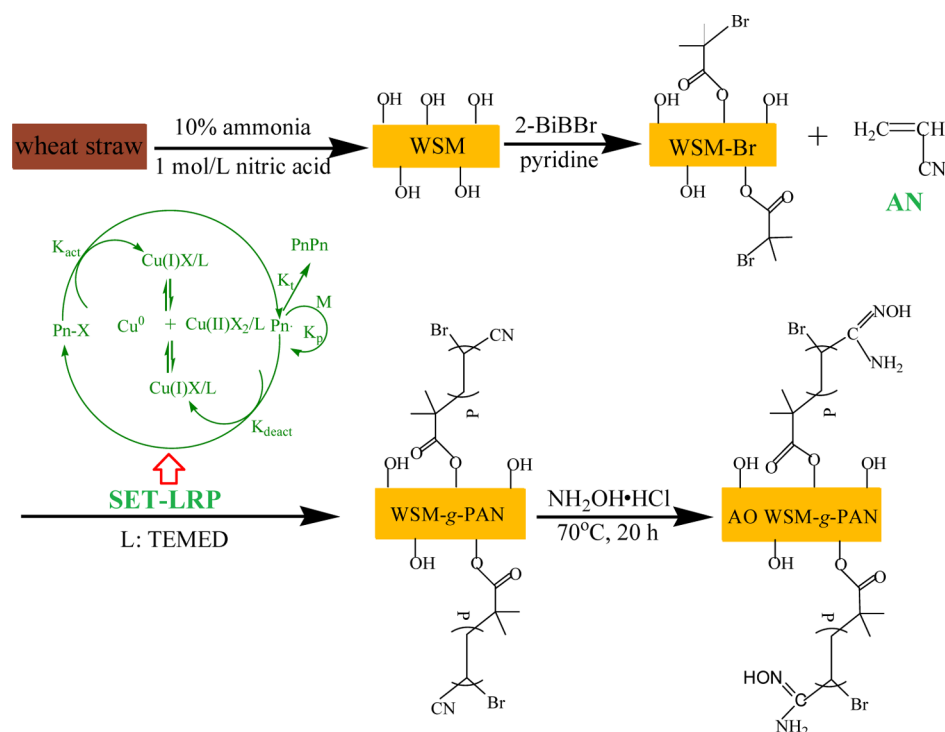


Figure 1. Synthetic routes for preparation AO WSM-g-PAN.

wheat straw matrix-*g*-polyacrylonitrile (AO WSM-*g*-PAN) was prepared by SET-LRP and a modification process that introduced amidoxime groups onto the surface of wheat straw. The primary objective is to prepare a novel adsorbent using SET-LRP and determine the adsorption properties in selectivity and adsorption capacity. Due to the high efficiency and selectivity, AO WSM-*g*-PAN is considered to be a specific adsorbent to remove Hg(II). Thus, the adsorption properties of wheat straw can be enhanced and tailored by introducing different functional groups, demonstrating a step toward the preparation of specific adsorbents.

## EXPERIMENTAL SECTION

**Materials.** Wheat straw was collected from Jining, Shandong Province (China). Acrylonitrile (AN) was bought from Fuchen Chemical Reagents (Tianjin, China), which was distilled under normal pressure and stored in a refrigerator. Cu powder (analytical grade) and *N,N*-dimethylformamide (DMF, analytical grade) were obtained from Tianjin Chemical Reagents. 2-Bromoisobutyl bromide (2-BiBBr), pyridine, and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were supplied by Aladdin Chemistry and used as received.

**Synthesis of Wheat Straw Macroinitiator.** *Pretreatment of Wheat Straw.* Wheat straw was pretreated by ammonia and nitric acid according to Liu's method.<sup>10</sup> Washed and dried wheat straw was smashed and sifted. A total of 2.5 g of wheat straw powder was soaked in 82 mL 10% ammonia for 48 h at room temperature. After a definite time, the mixture was filtered and washed with distilled water many times. Then, the filtered substance was immersed in 450 mL of 1 mol/L nitric acid and stirred at 90 °C for 45 min. Finally, the mixture was washed, filtered, and dried at 50 °C, obtaining a wheat straw matrix (WSM).

*Immobilization of SET-LRP Initiator on WSM Surface.* A total of 2.5 g of WSM was immersed in 50 mL DMF and ultrasonicated for 20 min before use. The mixture was cooled in ice water under nitrogen atmosphere for 30 min. Then, 5 mL of pyridine was injected using a syringe, and 5 mL of 2-BiBBr dissolved in 10 mL DMF was added dropwise. The mixture was stirred for 24 h at room temperature, followed by precipitation in ethanol and washing with distilled water.

Finally, the residue was dried at 25 °C and named as macroinitiator WSM-Br.

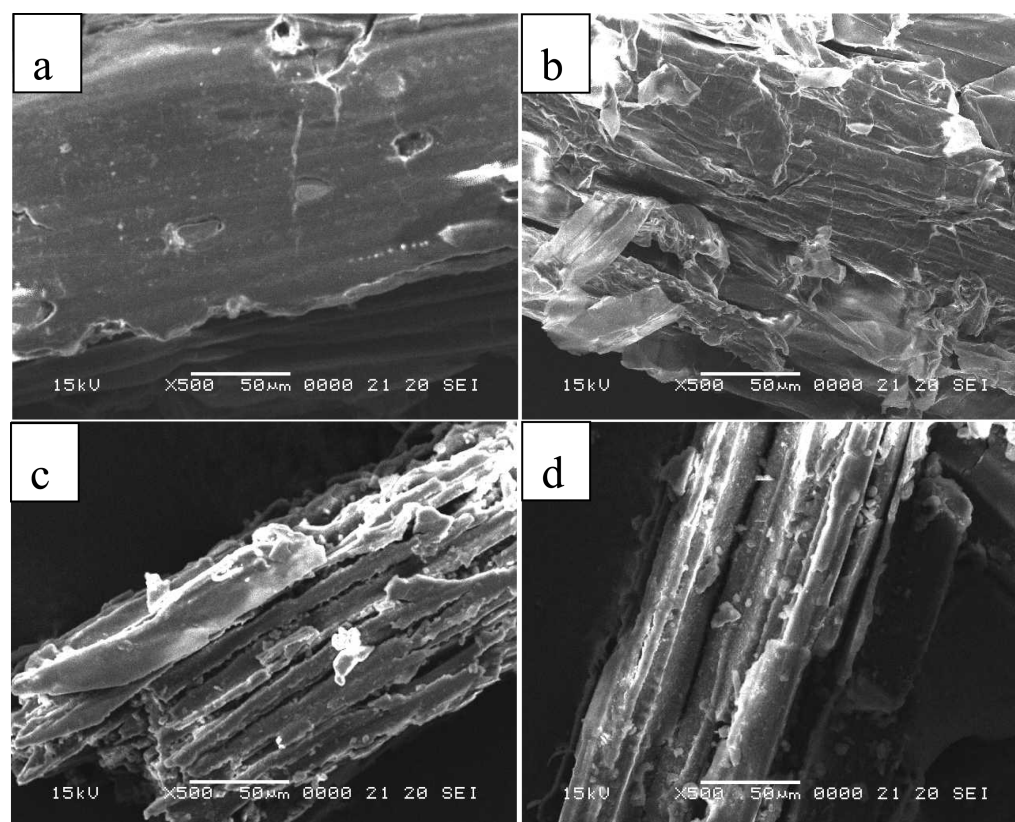
**Surface Polymerization of Acrylonitrile Using WSM-Br by SET-LRP.** In a typical procedure, Cu powder (0.02 g, 0.38 mmol) and TEMED (88.1  $\mu$ L, 0.76 mmol) were mixed in 10 mL of DMF in a two-necked flask, and the mixture was bubbled with N<sub>2</sub> for 10 min. Then, dried macroinitiator WSM-Br (0.8 g) and AN (10 mL, 151.9 mmol) were successively added into the flask. The mixture in the flask was degassed three times and then stirred under nitrogen atmosphere in an oil bath of 65 °C for 24 h. After a definite time, the sample was washed with a mixed solution of methanol/water (V:V=1:1), precipitated for 24 h, and then separated by filtration. Finally, the sample was dried until a constant weight at 50 °C and was referred to as the graft copolymer wheat straw matrix-*g*-polyacrylonitrile (WSM-*g*-PAN).

**Preparation of Adsorbent Based on WSM-*g*-PAN.** A total of 2.0 g of WSM-*g*-PAN and 3.0 g of hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) were added to 20 mL of methanol and then stirred under reflux condensing for 2 h. Sodium hydroxide solution was added to adjust the pH of the mixture to be 9.0. The mixture was stirred at 70 °C for 20 h, filtered, extracted for 12 h in ethanol, and dried at 50 °C.<sup>25,26</sup> Finally, the adsorbent AO WSM-*g*-PAN was obtained.

**Effect of pH on Adsorption.** The adsorption properties of WSM and AO WSM-*g*-PAN to Hg(II) were determined by batch experiments. A total of 10 mg of adsorbent was shaken in 20 mL of a 5  $\times$  10<sup>-3</sup> mol/L Hg(II) solution with different pH at 25 °C for 24 h. Then, 4 mL of solution was extracted and diluted to 25 mL with distilled water. The concentrations of Hg(II) ions were detected via a GBC-932 atomic adsorption spectrophotometer (AAS).

**Adsorption Selectivity.** The selectivity experiments were performed in a 100 mL flask contained 10 mg of adsorbent AO WSM-*g*-PAN, 1 mL of a 0.1 mol/L Hg(II) solution, 1 mL of a 0.1 mol/L coexisting metal ions solution, and an 18 mL buffer solution with pH 6.0. Then, the flask was shaken for 24 h at 25 °C. The concentrations of Hg(II) and coexisting metal ions were detected by AAS.

**Characterization.** The conversion of AN was measured by gravimetry. Fourier transform infrared (FTIR) spectroscopy was recorded on a Nicolet MAGNAIR550 spectrophotometer, which was used to detect the functional groups on the surface of samples. The surface morphologies of wheat straw-based samples were examined by



**Figure 2.** SEM images of samples (a, wheat straw; b, WSM; c, WSM-g-PAN; and d, AO WSM-g-PAN).

scanning electron microscopy (SEM). Atomic adsorption analysis of different metal ions was carried out on a 932B atomic adsorption spectrophotometer (AAS). Thermogravimetric (TG) curves of WSM and AO WSM-g-PAN were analyzed on a Netzsch STA 409. The contents of C, H, N, and S were determined by Vario EL cube elemental analyzer with analytical precision for C, H, N, and S  $\leq 0.1\%$ .

## RESULTS AND DISCUSSION

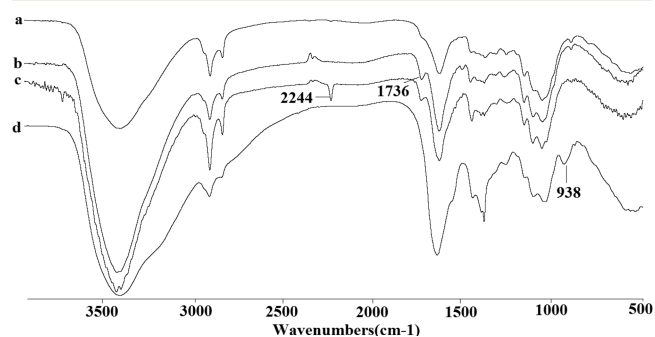
The synthetic routes of AO WSM-g-PAN are presented in Figure 1 and corresponding processes were illustrated as follows: (1) Wheat straw was treated by ammonia and nitric acid to yield WSM. (2) Macroinitiator WSM-Br was prepared by direct acylation of WSM with 2-bromoisobutryl bromide. (3) The graft copolymer WSM-g-PAN was synthesized by SET-LRP with WSM-Br as initiator. (4) WSM-g-PAN was modified by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to prepare specific adsorbent AO WSM-g-PAN.

**Pretreatment of Wheat Straw and Preparation of WSM-Br.** Wheat straw cannot directly react with chemical moieties because the cellulose are covered by some impurities, such as hemicelluloses, lignin, pectin, and wax. Moreover, huge numbers of hydroxyl groups existing in cellulose form intermolecular hydrogen bonds. The existence of intermolecular hydrogen bonds not only decreases the reactivity of hydroxyl groups but also reduces the adsorption capacities of WS for metal ions.<sup>27</sup> Therefore, it is necessary to treat wheat straw with ammonia and nitric acid in order to remove the impurities that dissolve partly in lye and obtain a high reactivity matrix that contains high percentage cellulose. SEM analyses were conducted to observe the surface morphology of the wheat straw before and after pretreatment. SEM images of wheat straw (a) and WSM (b) were presented in Figure 2 and indicated that the wheat straw structural and morphological

integrity had been largely changed after pretreatment. The morphology change might be ascribed to the remove of wax on the surface and dissolution of part hemicellulose and lignin.

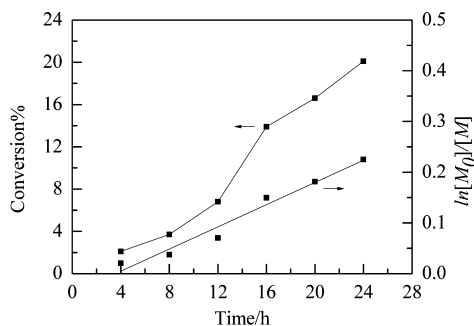
The macroinitiator WSM-Br was prepared by partial acylation of WSM hydroxyl groups using 2-BiBB. In order to achieve a moderate substitution degree, an excess of 2-BiBB was necessary. The functionalization of WSM with 2-BiBB was qualitatively confirmed by FTIR. Compared with spectra of WSM (Figure 3a), a new band at 1736  $\text{cm}^{-1}$  in Figure 3b was attributed to the carbonyl vibration of ester groups in WSM-Br, which demonstrated the success of the partial acylation of WSM.

**Grafting of AN from Macroinitiator WSM-Br.** The grafting of AN from initiator-functionalized WSM via SET-LRP was proceeded using the molar ratio of  $[\text{AN}]_0:[\text{Cu}]_0:[\text{TEMED}]_0$  at 200:0.5:1, and the drained weight of macroinitiator WSM-Br was 0.8 g. Six parallel experiments



**Figure 3.** FTIR spectra of samples (a, WSM; b, WSM-Br; c, WSM-g-PAN; and d, AO WSM-g-PAN).

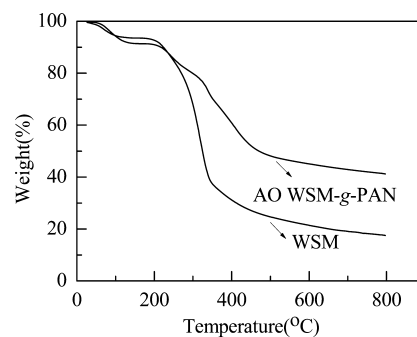
were performed and run for different time intervals ranging from 4 to 24 h. As illustrated in Figure 4, the semilogarithmic



**Figure 4.** Kinetic plots for SET-LRP of AN at 65 °C in DMF with  $[AN]_0 = 7.60$  mol/L,  $[AN]_0:[Cu]_0:[TEMED]_0 = 200:0.5:1$ , and  $m_{WSM-Br} = 0.8$  g.

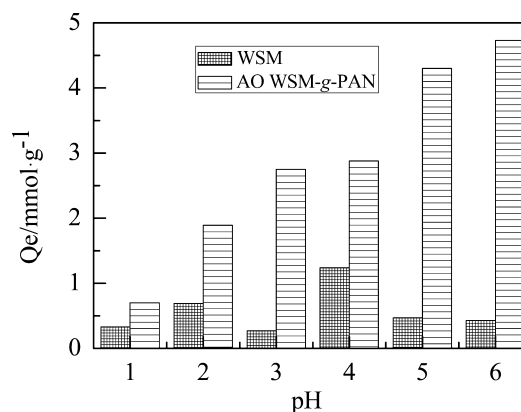
kinetic plot was approximately linear and manifested that the polymerization followed first-order kinetics. The long induction period of polymerization might be ascribed to the low concentration of dormant species immobilized on the surface, which was caused by limited available surface area and steric hindrance induced by a cellulose backbone in the heterogeneous reaction. To confirm successful grafting polymerization, the copolymer WSM-g-PAN was characterized by FTIR and SEM. After grafting polymerization, cyano groups of AN were introduced into the surface of WSM, which could be proven by the emergence of new peaks of cyano groups at  $2244\text{ cm}^{-1}$  in Figure 3c. Figure 2c also exhibits a more loose surface structure of WSM-g-PAN compared to WSM (Figure 2b) and wheat straw (Figure 2a). The contents of nitrogen (N%) and carbon (C%) of WSM-g-PAN were 17.29% and 59.74%, respectively. However, WSM had only 0.52% nitrogen (N%) and 42.82% carbon (C%). The results were agreement with the results of FTIR and SEM.

**Preparation of Agricultural Residue Adsorbent.** The adsorbent was prepared by modifying WSM-g-PAN with  $NH_2OH \cdot HCl$ , which converted cyano groups of WSM-g-PAN to amidoxime groups. Figure 3 showed FTIR spectra of WSM-g-PAN (c) and AO WSM-g-PAN (d). By comparison with the two curves, the bands at  $2244\text{ cm}^{-1}$  disappeared and a new peak at  $938\text{ cm}^{-1}$  appeared, which were the characteristic peaks of cyano and amidoxime groups, respectively, indicating that cyano groups were converted to amidoxime groups successfully. The appearance of amidoxime groups on the adsorbent played an important role in the  $Hg(II)$  binding process. The morphology of AO WSM-g-PAN was similar to WSM-g-PAN as revealed in Figure 2d, which also has a more loose structure. The existence of the loose structure is beneficial to the adsorption of metal ions. Thermal degradation behaviors of the prepared adsorbents were detected by TGA, and the plots of WSM and AO WSM-g-PAN are shown in Figure 5. The initial degradation of the two samples between 50 and  $100\text{ °C}$  was attributed to in situ formation acid on cellulose. With the temperature increasing, WSM had a representative degradation behavior of cellulose at  $260\text{ °C}$  due to sulfuric acid hydrolysis.<sup>28</sup> As illustrated in Figure 5, the major second decomposition peaks of WSM and AO WSM-g-PAN occurred at  $260\text{--}350\text{ °C}$  (mass loss 60–62%) and  $260\text{--}450\text{ °C}$  (mass loss 45–47%), respectively. The lower mass loss of AO WSM-g-PAN indicated that it had a higher thermal stability than adsorbent WSM.<sup>27</sup>



**Figure 5.** TGA plots of WSM and AO WSM-g-PAN.

**Effect of pH on Adsorption.** AO WSM-g-PAN could form stable chelating compounds with metal ions by amidoxime groups and hydroxyl groups. Figure 6 showed the saturated



**Figure 6.** Saturated adsorption capacities of WSM and AO WSM-g-PAN for  $Hg(II)$  at different pH values.

adsorption capacities of WSM and AO WSM-g-PAN for  $Hg(II)$  at different pH. Figure 6 exhibited different variation tendencies of adsorption of WSM and AO WSM-g-PAN. It showed that the adsorption process of AO WSM-g-PAN was pH dependent, and the adsorption capacity increased as the pH of the solution increased from 1.0 to 6.0. However, the adsorption capacity of WSM increased with an increase in pH from 1.0 to 4.0 and then decreased. It was obviously that AO WSM-g-PAN had a superior adsorption capacity to WSM for  $Hg(II)$ , and the highest adsorption capacity was  $4.7\text{ mmol g}^{-1}$  at pH 6.0. These phenomena might be ascribed to different existent states of adsorbent surface charge and metal ions at different pH. At low solution pH, the functional groups on the adsorbent surface are protonated and positively charged, which is not beneficial to the metal adsorption. With an increase in pH, the protonated functional groups would be deprotonated, which could enhance electrostatic attraction between adsorbent and metal ions. The high adsorption of AO WSM-g-PAN further demonstrated that the chelating effect of amidoxime groups and the loose structure played important roles in adsorption.

**Adsorption Selectivity.** The adsorption selectivity of AO WSM-g-PAN was explored by five binary metal ions systems, and the adsorption results are summarized in Table 1. As shown in Table 1,  $Hg(II)$  was easily adsorbed by AO WSM-g-PAN from the systems of  $Hg(II)\text{--}Pb(II)$ ,  $Hg(II)\text{--}Ni(II)$ ,  $Hg(II)\text{--}Zn(II)$ ,  $Hg(II)\text{--}Cu(II)$ , and  $Hg(II)\text{--}Ag(I)$ , and the high selective coefficients indicated that AO WSM-g-PAN had excellent selectivity for  $Hg(II)$ . These phenomena could be

**Table 1.** Adsorption Selectivity of AO WSM-g-PAN for Hg(II)

system	metal ions	adsorption capacities (mmol/g)	selective coefficient <sup>a</sup>
Hg(II)–Pb(II)	Hg(II)	4.13	41.3
	Pb(II)	0.10	
Hg(II)–Cu(II)	Hg(II)	2.14	30.6
	Cu(II)	0.07	
Hg(II)–Ag(I)	Hg(II)	1.81	20.1
	Ag(I)	0.09	
Hg(II)–Ni(II)	Hg(II)	4.78	∞
	Ni(II)	0	
Hg(II)–Zn(II)	Hg(II)	3.26	∞
	Zn(II)	0	

<sup>a</sup>The selectivity coefficient is the ratio of adsorption capacities of metal ions in binary mixtures.

attributed to the high affinity of Hg(II) ions for oxime and amine groups of the adsorbent. According to the hard–soft acid–base theory, Hg(II) is defined as a soft ion that can form a relatively stable complex with groups containing nitrogen and sulfur atoms.<sup>29</sup> Table 1 also displayed the relatively low selective coefficient of AO WSM-g-PAN in the Hg(II)–Ag(I) system. This is because Ag(I) also belongs to soft acids. Therefore, AO WSM-g-PAN exhibited a superior adsorption capacity to Hg(II) and could probably be applied to separate Hg(II) from a multi-ionic aqueous solution.

## CONCLUSIONS

A novel agricultural residue adsorbent amidoxime wheat straw matrix-g-polyacrylonitrile with an irregular surface, loose structure, and high stability was successfully prepared by a single-electron transfer-living radical polymerization and modification process. Wheat straw functionalized with amidoxime groups showed a superior adsorption capacity in comparison to wheat straw and high selectivity for Hg(II) from binary ion systems in the existence of Ni(II), Pb(II), Cu(II), Zn(II), and Ag(I). Tailored agricultural residue surface functionalization might be employed to increase the heavy metal ion adsorption amount and species by a specific design.

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### Notes

The authors declare no competing financial interest.

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