

Research Article

Effect of Alkali Treatment of Wheat Straw on Adsorption of Cu(II) under Acidic Condition

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The convenient and feasible pretreatment method of alkali treatment is very common in the degradation process of wheat straw. However, its utilization in the pretreatment of wheat straw as alternative adsorbents for aqueous heavy metals remediation is rarely reported. The present study investigated the removal efficiency of Cu(II) ions using wheat straw with alkali pretreatment. The condition of alkali treatment on wheat straw was optimized with the adsorption capacity of Cu(II) as indicator using single-factor experiments. The influences of wheat straw dosages, pH values, contact time, and temperatures on adsorption performance for both untreated wheat straw (UWS) and alkali-treated wheat straw (AWS) were investigated. Results showed that the relatively large removal rate of Cu(II) could be obtained, and chemical behavior occurred during the adsorption process. Characteristic analysis found that the major function of alkali treatment to wheat straw was to introduce the hydroxy group, which resulted in the increase of -C-O- group. Although the adsorption capacity is not as high as the one of ligands supported adsorbents, the method is easy to operate and has a wide range of application; at the same time, it could realize both purposes of treating heavy metal pollution and solid wastes.

1. Introduction

Copper (Cu), a redox active metal element, usually exists as monovalent copper [Cu(I)] or bivalent copper [Cu(II)] in natural and industrial waters. Cu(I) is commonly found in the form of cuprous complex ions; when cuprous complex ions decompose in the acidic environment, the Cu(I) could change into Cu(II) spontaneously through disproportionation reaction [1]. Sources of copper ion waste include printing and dyeing industry, electroplating, nonferrous metal mining and metallurgy, and electronic materials rinse [2, 3]. Copper ion is well known to be one of the required metal elements for human body because it is component of hemoglobin synthesis, affecting endocrine glands function. However, excess copper ion would damage vital organs such as liver, kidneys, brain, and stomach and cause serious disease. It was reported that the safe concentration of Cu(II) on carp was only 0.7 mg/L in aqueous and the maximum permissible limit of Cu(II) in drinking water is 1.3 mg/L by WHO [4, 5].

Various methods have been used to treat copper ion contaminated water, including coprecipitation, adsorption, electrochemical precipitation, ion exchange, membrane separation, and biological treatment [6]. Among these methods, adsorption in ion exchange and complexation with high sorption efficiency is considered as one of the most effective techniques based on easy recovery of metals and the possibility to reuse the adsorbent [7, 8]. A wide range of adsorbents including resin, clay, activated carbon, and synthetic mesoporous organosilicas have been extensively used for Cu(II) ion removal [9–11]. In addition, many nanomaterials such as graphene or graphene oxide, carbon nanotubes, nanoparticles, biosorbents, polymers, and porous- or layer-structured minerals are developed for metal removal efficiency due to high s/v ratios [12–14]. Therein, the ligand based nanoporous materials with high surface area and large pore volume have advantages in the field of metal adsorption and separation in second generation solid-liquid processes [15, 16]. Awwal et al. prepared various ligand based materials

for metal ions detection and removal, and the nanomaterials were exhibited intrinsic properties from the stand point sensitivity and selectivity as well as excellent adsorption capacity [17–20]; at the same time, the limit of metal ions detection was calculated to be $0.15 \mu\text{g/L}$, and the methods is obviously much simpler and greener than some conventional comprising multistep processes [21, 22].

Besides the above adsorbents, there is one kind of adsorbent derived from biomass, especially agricultural residues because natural cellulose inside has better hydrophilicity and porous structure [23]. One advantage of this kind of adsorbent is that it comes from recycled waste resources, and the measure could play a role of killing two birds with one stone, so it is attracting some interests [24]. As the best-known agricultural residues, the straw and stalks have been chosen to adsorb various harmful heavy metals and organic wastes by more and more researchers in recent years. The adsorbate removal rates of raw straw and stalks were just around 20%~40% [25, 26]. In order to improve the adsorption efficiency, the modification of straw and stalks has become the key point. In fact, pretreatment has been the key challenge in the field of straw and stalks application for a long time, and a wide variety of methods have been studied including physical pretreatment such as ammonia explosion, steam explosion, and ultrasonic or microwave treatment; chemical pretreatment such as the use of acid and alkali, zinc chloride, and amine; and biological pretreatment [27]. When it comes to modification of straw and stalks for adsorption, most methods were focused on the preparation of biochar by high temperatures pyrolysis or cationic/anion adsorbent through chemical reactions such as esterification, oxidation, graft copolymerization, and cross linking reaction, which could enhance the adsorption capacity by introducing some special functional groups such as amine groups and carboxyl groups to straw and stalks [28, 29]. For example, Gong et al. utilized esterifying mercaptoacetic acid to prepare thiol wheat straw for the removal of Hg(II) [30], and Chen et al. used diethylenetriamine as modifying agent to react with corn stalks in the presence of DMF to improve adsorbent ability [31]. Alkali treatment is the most common method in the pretreatment of cellulose, and many studies showed that it could increase the reaction sites and improve the swelling capacity [32, 33]. What is more important is that the alkali treatment of straw and stalks is convenient and feasible. Weng et al. utilized pressure steam and base (NaOH) to treat black tea power for the removal of Cu(II) and the maximum adsorption capacity of 43.18 mg/g at pH 4.4 while a nearly 90% Cu removal after 10 min of contact period was obtained [34]. And Sun et al. used KOH modified hydrochars from different feedstocks for enhanced removal of heavy metals from water, and the increased cadmium sorption capacity of $30.40\text{--}40.78 \text{ mg/g}$ compared to that of unmodified hydrochars of $13.92\text{--}14.52 \text{ mg/g}$ was obtained [35]. However, there was little research about the alkali treatment directly on the straw and stalks for the adsorption effects of heavy metals.

In this paper sodium hydroxide was used to treat wheat straw directly to absorb Cu(II). Factors such as the concentration of NaOH, wheat straw dosage, pH values, and temperature were investigated and made a comparison between UWS

and AWS. The potential use of this modified wheat straw in the adsorption of Cu(II) was investigated under kinetic and equilibrium conditions. The rate of adsorption, adsorption capacity, and adsorption mechanism of Cu(II) adsorption onto AWS were determined by a number of kinetic and adsorption isotherm models. The thermodynamic parameters were also used to detect the adsorption behavior. At the same time, scanning electron micrographs (SEM) and Fourier transform infrared spectroscopy (FTIR) were utilized for identifying the characteristics of Cu(II) adsorption onto AWS.

2. Materials and Methods

2.1. Materials. The raw wheat straw was collected from the suburb of Zhengzhou city, China. The materials were washed and soaked with deionized water and then dried at 80°C for 24 h. After that they were ground and passed 40-mesh screen. The sieved wheat straw was immersed in the solution of NaOH for some time and then the product was washed with 1% HCl and deionized water until the eluent reached neutral followed by drying at 80°C for 24 h, passing 40-mesh screen again. The final AWS was stored in a desiccator for further use in all the experiments.

All the primary chemicals used in this study were analytical grade and used without further purification. The stock solution of 1000 mg/L Cu(II) was prepared by dissolving 2.5 g anhydrous cupric sulfate in 1000 mL deionized water. All required concentrations were prepared by diluting the stock standard solution.

2.2. The Adsorption Experiments of Cu(II). Adsorption experiments were performed by the batch method, in which a given dosage of UWS/AWS was taken into 100 mL conical flask with 50 mL solution of known Cu(II) concentration. The flasks were shaken in a thermostatic box at a rate of 150 rpm for certain time. The temperature was kept within $\pm 1^\circ\text{C}$ of the desired values in all the experiments. After equilibrium, the samples were withdrawn and filtered through a $0.45 \mu\text{m}$ membrane filter. The Cu(II) ions in the filtrate were measured using an atomic absorption spectrophotometer (WFX-110A) [40]. The experimental procedure conducted for studying kinetics of Cu(II) adsorption was the same as described above except the different contacting time intervals. Each batch experiment was conducted in triplicate, and the average values were taken in the data analysis.

The adsorption capacity at any time (q_t) and removal rate (Re) were calculated by the following equations:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

$$\text{Re} = \frac{(C_0 - C_t)}{C_0} \times 100\%,$$

where C_0 (mg/L) is the initial concentration of Cu(II) in solution, C_t (mg/L) is the concentration of Cu(II) in solution at the time of t , V (L) is the volume of solution, and M (g) is the mass of adsorbent.

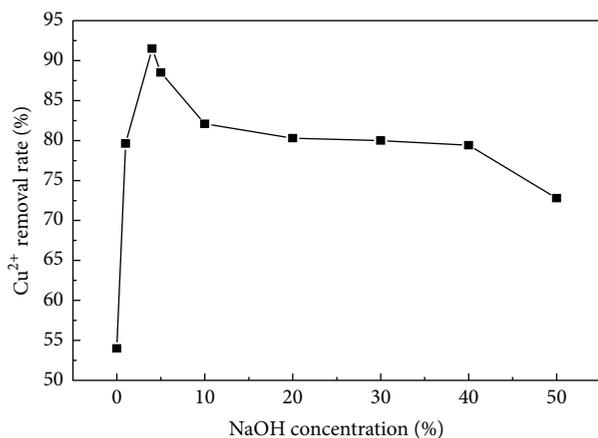


FIGURE 1: Effect of NaOH concentration (conditions: adsorbent dose = 5 g/L, adsorbate conc. = 20 mg/L, pH = 5, contact time = 6 h, temp. = $25 \pm 1^\circ\text{C}$, and stirring rate = 150 rpm).

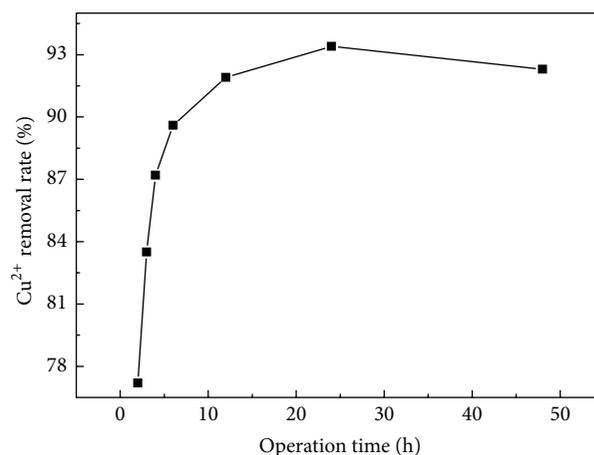


FIGURE 2: Effect of NaOH operation time (conditions: adsorbent dose = 5 g/L, adsorbate conc. = 20 mg/L, pH = 5, contact time = 6 h, temp. = $25 \pm 1^\circ\text{C}$, and stirring rate = 150 rpm).

3. Results and Discussion

3.1. The Effect of NaOH Concentration onto Wheat Straw for Cu(II) Removal. The modified conditions of NaOH concentration onto wheat straw for maximal Cu(II) removal were investigated and the results were shown in Figure 1. In Figure 1, raw wheat straw was modified by different concentrations of NaOH for 24 h firstly; after the product was washed and dried, experiments were carried out in 250 mL flask with the obtained AWS dosages of 5 g/L, Cu(II) concentration of 20 mg/L, pH values of 5.0, temperature of $25 \pm 1^\circ\text{C}$, and shaking speed of 150 rpm. As shown in Figure 1, when NaOH concentration was zero, that is, the untreated wheat straw (UWS), the Cu(II) removal rate was just 54.0%. When wheat straw was treated with 1% NaOH, it grew to 79.6%. The peak value of 91.5% appeared at NaOH concentration of 4%. After that, as NaOH concentration increased from 5% to 40%, the Cu(II) removal rate decreased gradually from 88.5% to 79.4%. When NaOH concentration continually increased to 50%, the Cu(II) removal rate of 72.8% appeared a relatively large drop. The reason for the decreased Cu(II) removal rate at high NaOH concentration should be that the massive NaOH resulted in violent hydrolysis of wheat straw, and the important adsorption component of cellulose in wheat straw was decomposed [41]. The result of optimal NaOH concentration of 4% was in accordance with the result in literature by the cooperative group of Barman et al. where 2% NaOH was supposed to be effective for reed straw pretreatment for structural changes [38], and the little difference came from the different straws.

3.2. The Effect of NaOH Operation Time onto Wheat Straw for Cu(II) Removal. The modified conditions of NaOH operation time onto wheat straw for maximal Cu(II) removal were investigated and the results were shown in Figure 2. It could be seen from Figure 2 that the Cu(II) removal rate improved a little when NaOH operation time changed from 3 h to 24 h and the data was from 83.5% to 93.4%, respectively. When it increased continually to 48 h, the Cu(II) removal rate

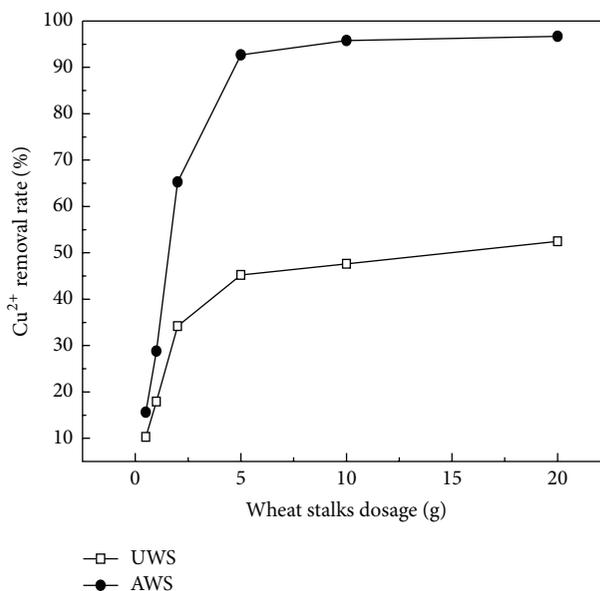


FIGURE 3: Effect of wheat stalks dosage (conditions: adsorbate conc. = 20 mg/L, pH = 5, contact time = 6 h, temp. = $25 \pm 1^\circ\text{C}$, and stirring rate = 150 rpm).

decreased a little. So the NaOH operation time on wheat straw should be no more than 24 h. And it could be found that the Cu(II) removal rate of wheat straw depended more on the NaOH concentration than on the NaOH operation time.

3.3. Effect of Adsorption Conditions on Wheat Straw for Cu(II) Removal. A series of adsorption conditions were studied to find the maximal potential of wheat straw for Cu(II) removal and the results were shown below.

3.3.1. Effect of Wheat Straw Dosages on Cu(II) Removal. The effect of UWS and AWS dosages on the adsorption of Cu(II) was shown in Figure 3. When the adsorbent concentration increased from 0.5 to 5 g/L, the Cu(II) removal rate of

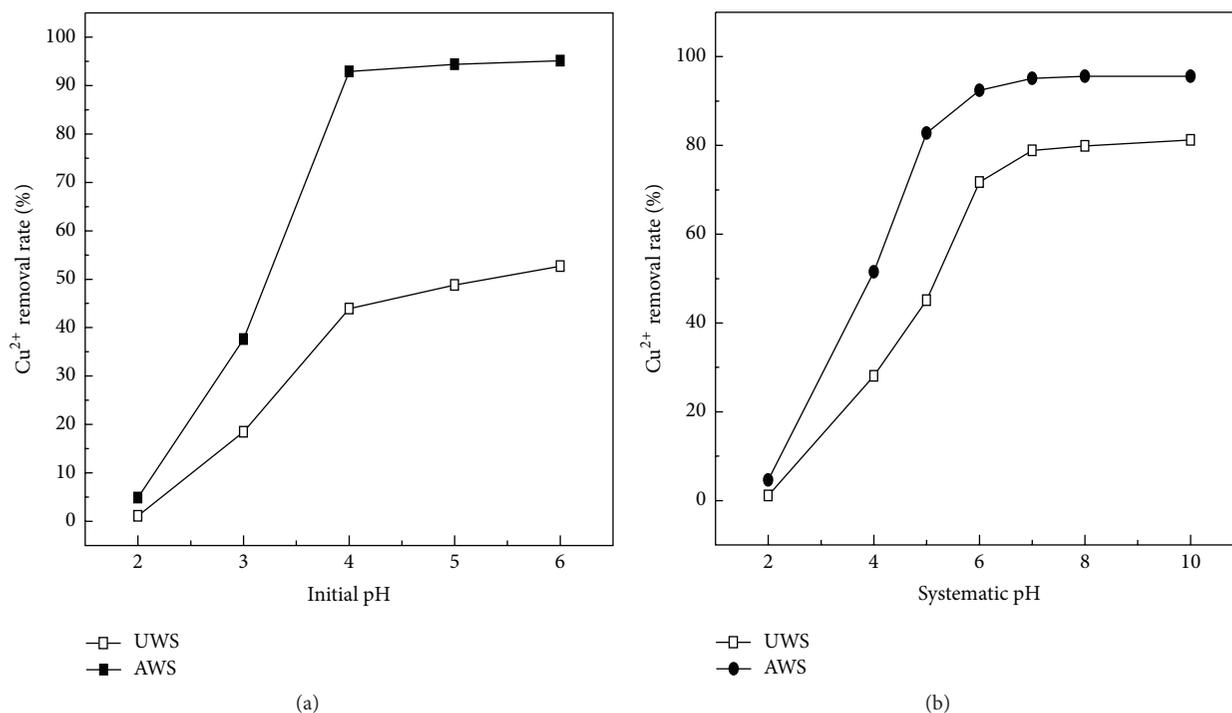


FIGURE 4: Effect of initial and systematic pH (conditions: adsorbent dose = 5 g/L, adsorbate conc. = 20 mg/L, contact time = 6 h, temp. = $25 \pm 1^\circ\text{C}$, and stirring rate = 150 rpm).

AWS increased significantly from 15.6% to 92.7% while the one of UWS was from 10.3% to 45.2%. After the critical dosage of 5 g/L, the Cu(II) removal rate increased very gently. Considering the inverse relationship of adsorption rate and adsorption capacity [42], the dosage of 5 g/L was chosen for later studies on Cu(II) removal. And the similar growth trends for both UWS and AWS implied that NaOH modification did not denature the wheat straw but just increased the reactions sites [34, 43].

3.3.2. Effect of Adsorption pH on Cu(II) Removal. The adsorption pH here was investigated through two ways. Figure 4(a) showed the effect of initial pH values on the adsorption of Cu(II) with both UWS and AWS, and in Figure 4(b) the system pH was adjusted to maintain a fixed value. In Figure 4(a), when the initial pH increased from 2.0 to 4.0, the Cu(II) removal rate of AWS increased significantly from 4.9% to 92.9% while that of UWS was from 1.1% to 43.9%. When the initial pH continually increased to 5.0 and 6.0, the Cu(II) removal rate improved very gently and the values of AWS were 94.4% and 95.1%, respectively, while those of UWS were 48.8% and 52.7%, respectively. In Figure 4(b), when the systematic pH increased from 2.0 to 6.0, the Cu(II) removal rate of AWS increased significantly from 4.6% to 92.4% while that of UWS was from 1.1% to 71.7%. When the system pH continually increased to 10.0, the Cu(II) removal rate of AWS was 95.6% while that of UWS was 81.2%, which was caused by adsorption and chemical precipitation. When the pH value is too high, the solution has the colloidal state and is not

easy for solid-liquid separation; at the same time it is not conducive to the regeneration of the adsorbent. According to precipitation calculation, the precipitation reaction of Cu(II) could happen when the pH value increased to 6.13 at Cu(II) concentration of 20 mg/L, so the Cu(II) removal rate rose greatly when system pH was beyond 6.0. It also could be found that the alkali treatment could observably enhance the adsorption capacity of wheat straw for the adsorption of Cu(II) even in the case of precipitation. However, in order to find the adsorption efficiency of alkali treatment on wheat straw for Cu(II) adsorption, the system pH value of 5.0 was chosen because it not only was close to the natural pH but also could eliminate the influence of precipitation.

3.3.3. Effect of Contact Time and Initial Concentration on Cu(II) Removal. The effect of contact time on the removal capacity of Cu(II) at various initial concentrations was described in Figure 5. As shown in Figure 5, the adsorption of Cu(II) was rapid initially and then slowed down till the attainment of equilibrium, and the slope reduced gradually when initial concentrations of Cu(II) increased from 5 mg/L to 50 mg/L. The equilibrium time was around 20 min for all of concentrations. The relatively fast adsorption of Cu(II) on the AWS probably reflected high accessibility of the Cu(II) ions to the active sites in the AWS. The percentage uptake of Cu(II) increased from 91.8% to 94.1% when initial Cu(II) concentrations increased from 5 mg/L to 10 mg/L. However, when initial Cu(II) concentrations improved continually to the data of 20 mg/L and 50 mg/L, the Cu(II) removal rates

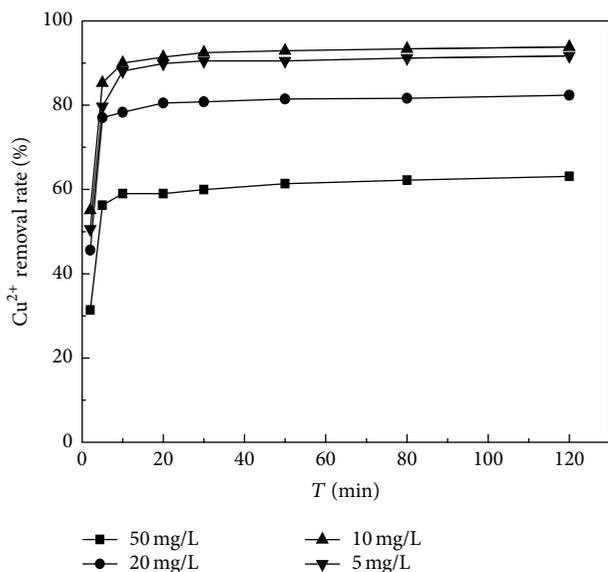


FIGURE 5: Effect of initial concentration and contact time on Cu(II) adsorption (conditions: adsorbent dose = 5 g/L, pH = 5, temp. = 25 ± 1 °C, and stirring rate = 150 rpm).

decreased to the data of 82.5% and 63.6%, respectively. The situation was expected because the total available adsorption sites were limited for the fixed adsorbent dosage [44].

3.4. Adsorption Isotherms. In order to find the optimal design of the adsorption system for the removal of adsorbate, it is necessary to establish the most appropriate correlation for the equilibrium data. In the study two important isotherms equations, namely, Langmuir and Freundlich isotherms, were utilized [45, 46]. Langmuir isotherm equation describes a monolayer adsorption, while Freundlich isotherm equation describes a multilayer adsorption and their forms were shown in the following:

$$\text{Langmuir isotherm } q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (2)$$

$$\text{Freundlich isotherm } q_e = k_F C_e^{1/n},$$

where q_e is the amount of the adsorbed adsorbate (mg/g) at equilibrium, q_m is the monolayer adsorption capacity of the adsorbent (mg/g), C_e is the concentration of adsorbate in the solution at equilibrium (mg/L), k_L is the Langmuir isotherm constant (L/mg) that is related to the adsorption energy, k_F is the Freundlich constant, and $1/n$ is the adsorption intensity.

Figure 6 depicted the experimental equilibrium data and the fitted equilibrium curve by Langmuir and Freundlich model for Cu(II) adsorption with UWS and AWS at temperatures of 288 K, 298 K, and 308 K, respectively.

The relative parameters of two equations were listed in Table 1. It could be seen from Table 1 that R^2 values for the Cu(II) adsorption using both UWS and AWS with Freundlich isotherm were higher ($R^2 > 0.98$) than the Langmuir equation. This result indicated that the Freundlich isotherm was most favorable for the adsorption of Cu(II) on

TABLE 1: Isotherm parameters obtained for the adsorption of Cu(II) onto wheat straw at different initial concentrations and temperature.

| Isotherm models | Isotherm parameters | | | | | |
|------------------|---------------------|--------|--------|--------|--------|--------|
| | UWS | | | AWS | | |
| T (K) | 288 | 298 | 308 | 288 | 298 | 308 |
| Langmuir | | | | | | |
| $q_{e,aqu}$ | 6.883 | 7.137 | 7.687 | 8.390 | 8.980 | 9.860 |
| q_{max} (mg/g) | 10.111 | 10.238 | 10.801 | 10.589 | 10.680 | 10.783 |
| k_L (L/mg) | 0.017 | 0.0187 | 0.0199 | 0.0316 | 0.0606 | 0.157 |
| R^2 | 0.993 | 0.994 | 0.984 | 0.993 | 0.979 | 0.966 |
| Freundlich | | | | | | |
| k_F (mg/g) | 0.421 | 0.475 | 0.537 | 0.824 | 1.747 | 1.998 |
| $1/n$ | 0.591 | 0.576 | 0.567 | 0.502 | 0.357 | 0.351 |
| R^2 | 0.994 | 0.993 | 0.992 | 0.995 | 0.987 | 0.984 |

the wheat straw, so the adsorption was multilayer [47]. And it also implied that NaOH modification did not denature the adsorption reaction of wheat straw with Cu(II) in aqueous solution. As shown in Table 1, Comparing with UWS, the adsorption capacity ($q_{e,aqu}$) of AWS increased to 21.9%, 25.8%, and 28.3%, respectively, when temperature was 288 K, 298 K, and 308 K, respectively. The results revealed that the convenient method of alkali treatment was effective in enhancing the adsorption capacity of wheat straw.

In order to get a further understanding of the adsorption mechanism, thermodynamic parameters such as free energy changes (ΔG), enthalpy changes (ΔH), and entropy changes (ΔS) were calculated and the formulas were listed sequentially as follows:

$$K_c = \frac{C_{ad,e}}{C_e} \quad (3)$$

$$\Delta G = -RT \ln K_c \quad (4)$$

$$\Delta G = \Delta H - T\Delta S, \quad (5)$$

where $C_{ad,e}$ is the concentration of adsorbate on the adsorbent at equilibrium (mg/L), C_e is the concentration of adsorbate in the solution at equilibrium (mg/L), K_c is the equilibrium constant, and R is the gas constant.

The thermodynamic parameters were shown in Table 2. ΔG values for both of UWS and AWS were negative, so the adsorption of Cu(II) on wheat straw was spontaneous. At the same time, ΔG values of Cu(II) adsorption on AWS were smaller than the ones of Cu(II) adsorption on UWS, which implied that the alkali treatment enhanced the adsorption reactions. The positive ΔS values indicated that the randomness was increased during the adsorption reactions, while the positive ΔH values validated that the Cu(II) adsorption on both UWS and AWS was endothermic.

3.5. Adsorption Kinetics. Adsorption kinetics models were also utilized to assist in finding the adsorption characteristics. Two models, namely, pseudo-first-order and pseudo-second-order models, were applied to obtain the best fitted model for

TABLE 2: Thermodynamic parameters for the adsorption of Cu(II).

| Temperature (K) | UWS | | | AWS | | |
|-----------------|---------------------|---------------------|-----------------------|---------------------|---------------------|-----------------------|
| | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (kJ/mol K) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (kJ/mol K) |
| 288 | -12.57 | 7.59 | 0.07 | -19.76 | 20.56 | 0.14 |
| 298 | -13.27 | 7.59 | 0.07 | -21.16 | 20.56 | 0.14 |
| 308 | -13.97 | 7.59 | 0.07 | -22.56 | 20.56 | 0.14 |

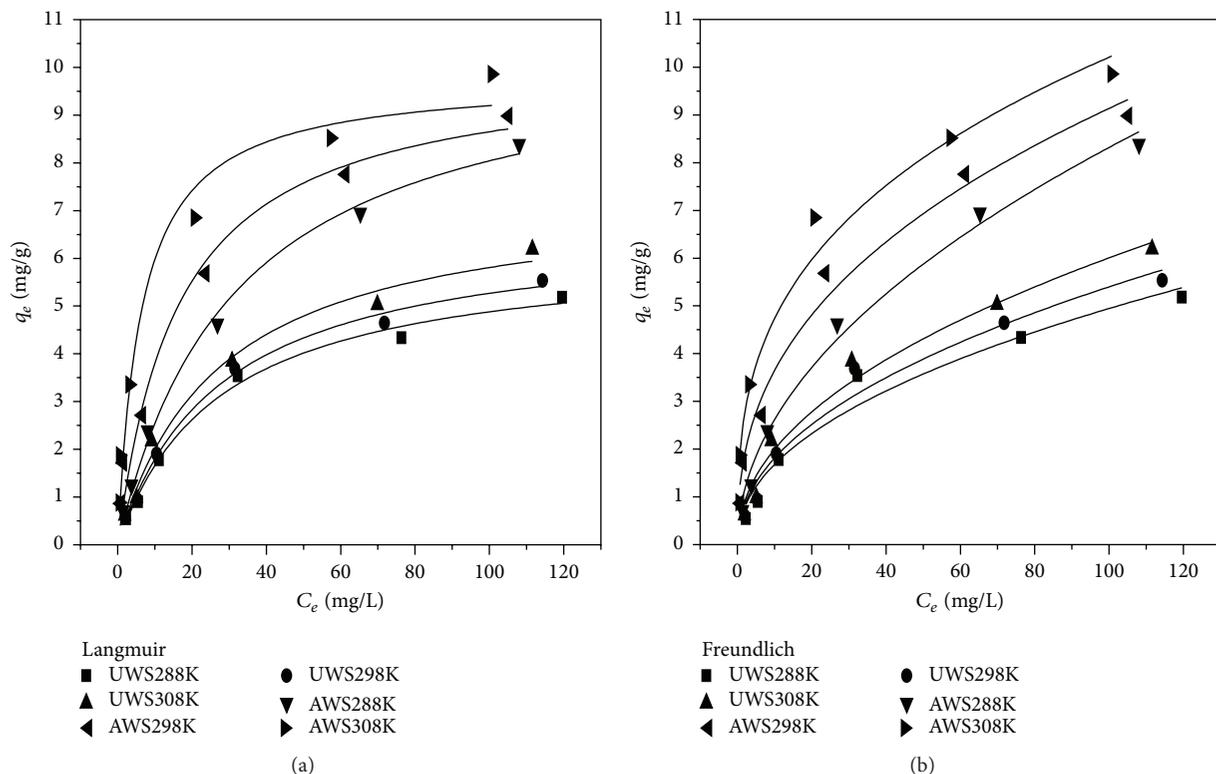


FIGURE 6: Langmuir and Freundlich adsorption isothermal curves of Cu(II) on wheat straw (conditions: adsorbent dose = 5 g/L, contact time = 6 h, pH = 5, and stirring rate = 150 rpm).

the experimental curve [36, 37], and their forms were shown as follows:

$$\text{Pseudo-first-order kinetic model } q_t = q_e (1 - e^{-k_1 t})$$

$$\text{Pseudo-second-order kinetic model } q_t = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)}, \quad (6)$$

where k_1 and k_2 are the rate constant of pseudo-first-order and pseudo-second-order kinetics models, respectively. q_e is the equilibrium adsorption capacity (mg/g).

Adsorption kinetics simulation curve was shown in Figure 7; the relative parameters of two equations were presented in Table 3. It could be seen from Figure 7 that q_e changed obviously along with the change of Cu(II) concentrations in aqueous solutions. And in Table 3 R^2 values for the Cu(II) adsorption on AWS with pseudo-second-order model were higher ($R^2 > 0.998$) than the pseudo-first-order model, and q_e values agreed well with the experimental data $q_{e,\text{exp}}$,

which indicated that the pseudo-second-order model was more suitable for simulation of the adsorption of Cu(II) on AWS, so chemical behavior occurred during the adsorption process.

3.6. Characteristics Analysis

3.6.1. SEM Analysis. The surface morphologies of UWS and AWS were observed using SEM and the pictures were shown in Figure 8. It could be seen from Figure 8 that the surface of RWS was incompact and coarse with many small particles attached, while the surface of AWS was much smoother and compact, which suggested that the order of cellulose was improved with alkali pretreatment, so the adsorption reaction was enhanced. The results were similar with several papers in which corn stalks were modified by organic reagents or NaOH [39, 48]. The reason should be that on the surface of straw and stalks some ash and extractible even amorphous substances exist which could be removed after the utilization

TABLE 3: Kinetic parameters for the adsorption of Cu(II) onto AWS at different initial concentrations.

| C_0 (mg/L) | $q_{e,exp}$ (mg/g) | Pseudo-first-order | | | Pseudo-second-order | | |
|--------------|--------------------|--------------------|-------|--------|---------------------|-------|--------|
| | | k_1 | q_e | R^2 | k_2 | q_e | R^2 |
| 5 | 0.917 | 0.419 | 0.906 | 0.9990 | 1.491 | 0.925 | 0.9994 |
| 10 | 1.876 | 0.503 | 1.850 | 0.9988 | 1.063 | 1.880 | 0.9999 |
| 20 | 3.295 | 0.594 | 3.237 | 0.9982 | 0.855 | 3.280 | 0.9997 |
| 50 | 6.747 | 0.522 | 6.512 | 0.9959 | 0.298 | 6.730 | 0.9984 |

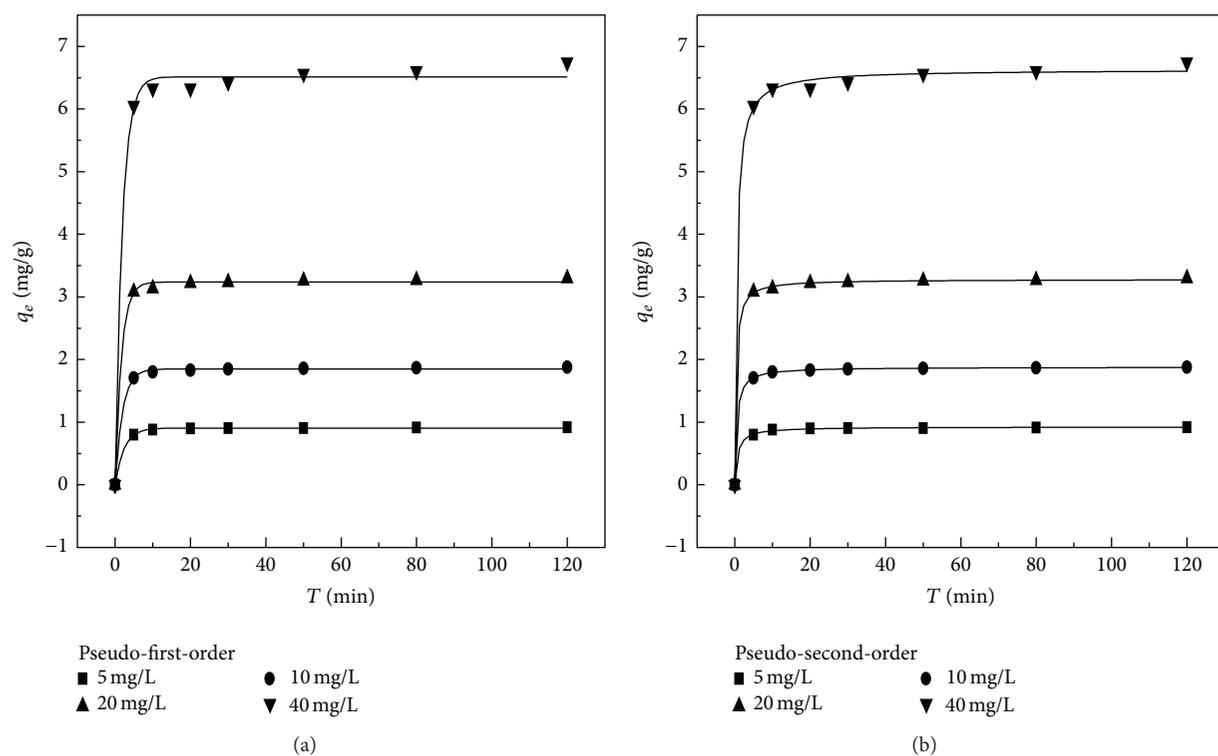
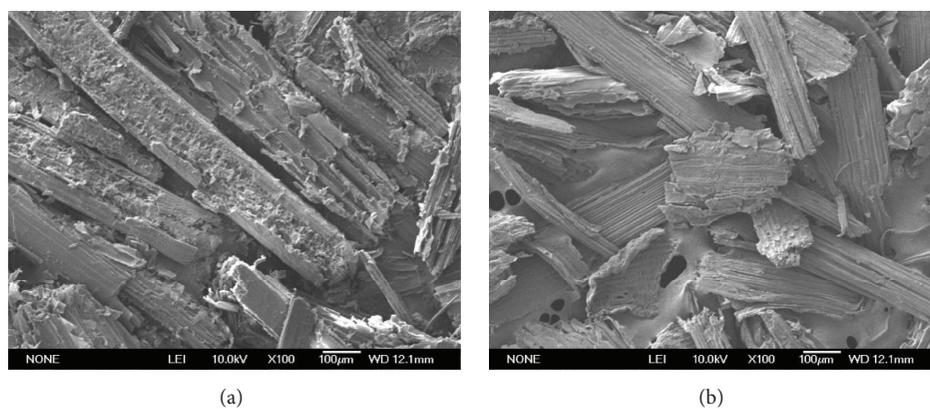
FIGURE 7: Pseudo-first-order and pseudo-second-order adsorption kinetics simulation curve of Cu(II) on AWS (conditions: adsorbent dose = 5 g/L, pH = 5, temp. = $25 \pm 1^\circ\text{C}$, and stirring rate = 150 rpm).

FIGURE 8: SEM of untreated wheat straw (UWS) (a) and alkali-treated wheat straw (AWS) (b).

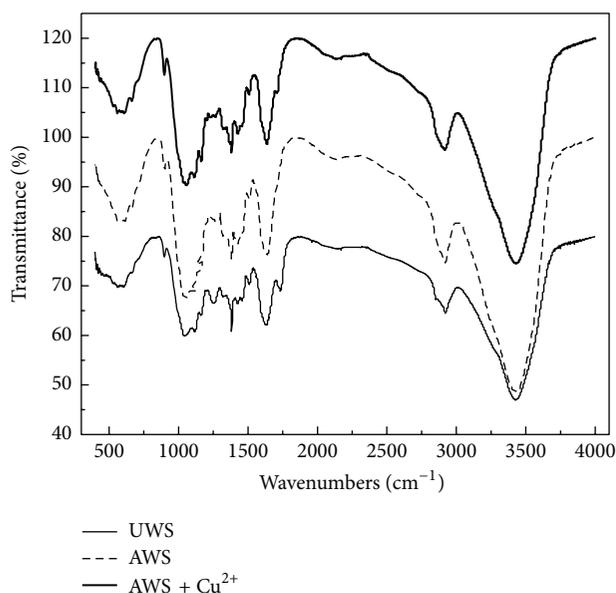


FIGURE 9: FTIR spectra of UWS and AWS and after adsorption of Cu(II) on AWS (AWS + Cu(II)).

of modifying agents, so the orderly structures of straw and stalks were revealed which helped the adsorption reactions.

3.6.2. FTIR Analysis. In order to identify the differences between UWS and AWS, FTIR analysis technique was utilized to distinguish some main characteristic functional groups in the absorbent. The infrared spectra of UWS, AWS, and AWS + Cu²⁺ (after adsorption of Cu²⁺ on AWS) were shown in Figure 9. In the UWS spectrum, the broad band observed at 3424.45 cm⁻¹ was the stretching vibration absorption peak of -OH group. And the adsorption bands at 2918.68 cm⁻¹ and 607.13 cm⁻¹ represented the stretching of C-H group, while the band at 1733.16 cm⁻¹ belonged to -C=O stretching vibration absorption peak and a little bit wide band at 1634.48 cm⁻¹ corresponded to the bending vibration of absorbed water. The band at 1253.53 cm⁻¹ indicated the antisymmetric stretching vibration absorption peak of -C-O-group. And the adsorption band at 897.66 cm⁻¹ represented the deformation peak of C-H group or bending vibration peak of -OH group. In the AWS spectrum, compared with the UWS spectrum, the band at 1733.16 cm⁻¹ caused by -C=O stretching vibration disappeared, which implied that the addition reaction maybe occurred in the -C=O group, and the band at 1253.53 cm⁻¹ caused by -C-O- group decomposed into two small peaks, which indicated that some substitution reaction took place on the side chain of -C-O- group [49]. So it could come to the conclusion that the enhanced adsorption capacity of wheat straw by alkali treatment resulted from the increase of ether bond. In the AWS + Cu²⁺ spectrum, the shift in the absorption band frequencies was observed, which suggested that the Cu(II) adsorption corresponded to the possible presence of functional groups on the absorbent. The Cu(II)-loaded spectrum further implied that the -C-O-group played an important role in the Cu(II) binding. Hence,

TABLE 4: Comparison of adsorption capacities of wheat straw for Cu(II) removal.

| Modification | pH | Q_m (mg/g) | Reference |
|----------------------------------|-----|--------------|------------|
| 4% NaOH | 5.0 | 10.05 | This study |
| 10% HNO ₃ and 1N NaOH | 6.0 | 11.43 | [36] |
| Hydrochars and 2 N KOH | 5.0 | 11.82 | [35] |
| Esterification | — | 39.17 | [37] |
| — | 5.0 | 7.05 | [38] |
| — | 4.5 | 5.0 | [39] |

it could draw the conclusion that the alkali treatment worked in the adsorption of wheat straw through the introduction of hydroxy which resulted in the increase of -C-O- group. This is in accordance with the conclusions in papers by Weng and Sun et al. where the hydroxy and oxygen-containing functional groups were introduced after the modification methods [34, 35].

3.7. Comparison of Various Treatment Methods of Wheat Straw for Cu(II) Adsorption. Table 4 demonstrates a comparison between maximum Cu(II) adsorption capacity by wheat straw and different pretreatment method from some papers, and “—” in the table represents that it was not mentioned in the reference or the wheat straw was untreated. It could be seen from Table 4 that except the higher Q_m value of 39.17 mg/g obtained from wheat straw with the pretreatment method of esterification [37], the Q_m of 10.78 mg/g in this study was just a little lower than the value of 11.82 mg/g obtained from the paper in which the method of hydrothermal carbonization and 2 N KOH was utilized [35]. In addition, the adsorption capacity increased with the rise of pH values, this is expected because of the precipitation effect. So the adsorption capacity obtained in this paper was acceptable, and because the modification method in this paper was not as complicated as other papers, and from the perspective of waste utilization as well as the accessible and feasible method, this study was meaningful.

4. Conclusions

The optimal alkali treatment conditions and adsorption conditions of wheat straw were investigated. Results showed that the optimal NaOH concentration and operation time were 4% and 24 h, respectively, and the dosage was chosen for 5 g/L, while the adsorption process was carried out at pH 5.0. The adsorption process of Cu(II) on AWS is fast and the optimum copper ion adsorption concentration is 10 mg/L. Freundlich isotherm was the most favorable for the adsorption of Cu(II) on the wheat straw, so the adsorption was multilayer. Comparing with UWS, the adsorption capacity of AUS increased to 21.9%, 25.8%, and 28.3%, respectively, when temperature was 288 K, 298 K, and 308 K. UWS and AWS adsorption of Cu(II) are a spontaneous exothermic process. The pseudo-second-order model was more suitable for simulation the adsorption of Cu(II) on AWS, so chemical behavior occurred during the adsorption process. Characteristic analysis found that the major function of alkali treatment

to wheat straw was to introduce the hydroxy group which resulted in the increase of -C-O- group. And here the alkali concentration should be no more than 4%, because excess alkali could decompose the functional groups in wheat straw. The results implied that the measure of straw returning to field did have effects on the heavy metal in soil and the application of alkali to wheat straw would strengthen this function. The adsorption and desorption of heavy metal by wheat straw would be the task which needed further study. In addition, the adsorption effects of alkali treatment wheat straw on other heavy metals such as Cr, Zn, and Hg as well as the ions selectivity should also be detected in the future work.

Competing Interests

The authors declare no conflict of interests.

Acknowledgments

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References

- [1] M. R. Awual, I. M. M. Rahman, T. Yaita, M. A. Khaleque, and M. Ferdows, "pH dependent Cu(II) and Pd(II) ions detection and removal from aqueous media by an efficient mesoporous adsorbent," *Chemical Engineering Journal*, vol. 236, pp. 100–109, 2014.
- [2] S. A. El-Safty, M. A. Shenashen, M. Ismael, M. Khairy, and M. R. Awual, "Optical mesosensors for monitoring and removal of ultra-trace concentration of Zn(II) and Cu(II) ions from water," *Analyst*, vol. 137, no. 22, pp. 5278–5290, 2012.
- [3] X. Zhao, L. B. Guo, and J. H. Qu, "Photoelectrocatalytic oxidation of Cu-EDTA complex and electrodeposition recovery of Cu in a continuous tubular photoelectrochemical reactor," *Chemical Engineering Journal*, vol. 239, pp. 53–59, 2014.
- [4] M. R. Awual, M. Ismael, T. Yaita et al., "Trace copper(II) ions detection and removal from water using novel ligand modified composite adsorbent," *Chemical Engineering Journal*, vol. 222, pp. 67–76, 2013.
- [5] Y. J. Xue, S. P. Wu, and M. Zhou, "Adsorption characterization of Cu(II) from aqueous solution onto basic oxygen furnace slag," *Chemical Engineering Journal*, vol. 231, pp. 355–364, 2013.
- [6] F.-R. Xiu, Y. Y. Qi, and F.-S. Zhang, "Co-treatment of waste printed circuit boards and polyvinyl chloride by subcritical water oxidation: removal of brominated flame retardants and recovery of Cu and Pb," *Chemical Engineering Journal*, vol. 237, pp. 242–249, 2014.
- [7] H. B. Liu, B. Y. Xu, M. M. Li, and X. C. Zhang, "Adsorption of aquatic cadmium (II) by modified wheat straw," *Technology of Water Treatment*, vol. 39, pp. 15–19, 2013.
- [8] S.-T. Yang, Y. Chang, H. Wang et al., "Folding/aggregation of graphene oxide and its application in Cu²⁺ removal," *Journal of Colloid and Interface Science*, vol. 351, no. 1, pp. 122–127, 2010.
- [9] M. Naushad, Z. A. AlOthman, M. R. Awual, M. M. Alam, and G. E. Eldesoky, "Adsorption kinetics, isotherms, and thermodynamic studies for the adsorption of Pb²⁺ and Hg²⁺ metal ions from aqueous medium using Ti(IV) iodovanadate cation exchanger," *Ionics*, vol. 21, no. 8, pp. 2237–2245, 2015.
- [10] M. Naushad, Z. A. AlOthman, M. M. Alam, M. R. Awual, G. E. Eldesoky, and M. Islam, "Synthesis of sodium dodecyl sulfate-supported nanocomposite cation exchanger: removal and recovery of Cu²⁺ from synthetic, pharmaceutical and alloy samples," *Journal of the Iranian Chemical Society*, vol. 12, no. 9, pp. 1677–1686, 2015.
- [11] B. W. Yu, J. Xu, J.-H. Liu et al., "Adsorption behavior of copper ions on graphene oxide-chitosan aerogel," *Journal of Environmental Chemical Engineering*, vol. 1, no. 4, pp. 1044–1050, 2013.
- [12] W. Sun, W. Pan, F. Wang, and N. Xu, "Removal of Se(IV) and Se(VI) by MFe₂O₄ nanoparticles from aqueous solution," *Chemical Engineering Journal*, vol. 273, pp. 353–362, 2015.
- [13] J. H. Doh, J. H. Kim, H. J. Kim, R. F. Ali, K. Shin, and Y. J. Hong, "Enhanced adsorption of aqueous copper(II) ions using dedoped poly-N-phenylglycine nanofibers," *Chemical Engineering Journal*, vol. 277, pp. 352–359, 2015.
- [14] N. Bakhtiari, S. Azizian, S. M. Alshehri, N. L. Torad, V. Malgras, and Y. Yamauchi, "Study on adsorption of copper ion from aqueous solution by MOF-derived nanoporous carbon," *Microporous and Mesoporous Materials*, vol. 217, article 7181, pp. 173–177, 2015.
- [15] M. R. Awual, "A novel facial composite adsorbent for enhanced copper(II) detection and removal from wastewater," *Chemical Engineering Journal*, vol. 266, pp. 368–375, 2015.
- [16] M. R. Awual, T. Yaita, S. A. El-Safty, H. Shiwaku, S. Suzuki, and Y. Okamoto, "Copper(II) ions capturing from water using ligand modified a new type mesoporous adsorbent," *Chemical Engineering Journal*, vol. 221, pp. 322–330, 2013.
- [17] M. R. Awual, G. E. Eldesoky, T. Yaita et al., "Schiff based ligand containing nano-composite adsorbent for optical copper(II) ions removal from aqueous solutions," *Chemical Engineering Journal*, vol. 279, pp. 639–647, 2015.
- [18] M. R. Awual and M. M. Hasanb, "Colorimetric detection and removal of copper(II) ions from wastewater samples using tailor-made composite adsorbent," *Sensors and Actuators B: Chemical*, vol. 206, pp. 692–700, 2015.
- [19] S. A. El-Safty, M. A. Shenashen, M. Ismael, M. Khairy, and M. R. Awual, "Mesoporous aluminosilica sensors for the visual removal and detection of Pd(II) and Cu(II) ions," *Microporous and Mesoporous Materials*, vol. 166, pp. 195–205, 2013.
- [20] M. R. Awual, T. Yaita, and Y. Okamoto, "A novel ligand based dual conjugate adsorbent for cobalt(II) and copper(II) ions capturing from water," *Sensors and Actuators B: Chemical*, vol. 203, pp. 71–80, 2014.
- [21] M. R. Awual, M. M. Hasan, M. A. Khaleque, and M. C. Sheikh, "Treatment of copper(II) containing wastewater by a newly developed ligand based facial conjugate materials," *Chemical Engineering Journal*, vol. 288, pp. 368–376, 2016.
- [22] M. R. Awual, M. Ismael, M. A. Khaleque, and T. Yaita, "Ultra-trace copper(II) detection and removal from wastewater using novel meso-adsorbent," *Journal of Industrial and Engineering Chemistry*, vol. 20, no. 4, pp. 2332–2340, 2014.
- [23] Y. Xiong, Z. H. Zhang, X. Wang, B. Liu, and J. Lin, "Hydrolysis of cellulose in ionic liquids catalyzed by a magnetically-recoverable solid acid catalyst," *Chemical Engineering Journal*, vol. 235, pp. 349–355, 2014.

- [24] X. Tan, B. Y. Gao, X. Xu et al., "Perchlorate uptake by wheat straw based adsorbent from aqueous solution and its subsequent biological regeneration," *Chemical Engineering Journal*, vol. 211-212, pp. 37-45, 2012.
- [25] X. Xu, B. Y. Gao, X. Tan et al., "Nitrate adsorption by stratified wheat straw resin in lab-scale columns," *Chemical Engineering Journal*, vol. 226, pp. 1-6, 2013.
- [26] Q.-Q. Zhong, Q.-Y. Yue, B.-Y. Gao, Q. Li, and X. Xu, "A novel amphoteric adsorbent derived from biomass materials: synthesis and adsorption for Cu(II)/Cr(VI) in single and binary systems," *Chemical Engineering Journal*, vol. 229, pp. 90-98, 2013.
- [27] M. Ertas, Q. Han, H. Jameel, and H.-M. Chang, "Enzymatic hydrolysis of autohydrolyzed wheat straw followed by refining to produce fermentable sugars," *Bioresource Technology*, vol. 152, pp. 259-266, 2014.
- [28] L. C. Zheng, C. F. Zhu, Z. Dang, H. Zhang, X. Yi, and C. Liu, "Preparation of cellulose derived from corn stalk and its application for cadmium ion adsorption from aqueous solution," *Carbohydrate Polymers*, vol. 90, no. 2, pp. 1008-1015, 2012.
- [29] S. Chen, Q. Yue, B. Gao, Q. Li, and X. Xu, "Preparation and characteristics of anion exchanger from corn stalks," *Desalination*, vol. 274, no. 1-3, pp. 113-119, 2011.
- [30] R. M. Gong, W. K. Cai, N. Li, J. A. Chen, J. J. Liang, and J. X. Cao, "Preparation and application of thiol wheat straw as sorbent for removing mercury ion from aqueous solution," *Desalination and Water Treatment*, vol. 21, no. 1-3, pp. 274-279, 2010.
- [31] S. H. Chen, Q. Y. Yue, B. Y. Gao, Q. Li, and X. Xu, "Removal of Cr(VI) from aqueous solution using modified corn stalks: characteristic, equilibrium, kinetic and thermodynamic study," *Chemical Engineering Journal*, vol. 168, no. 2, pp. 909-917, 2011.
- [32] M. Ishiguro and T. Endo, "Addition of alkali to the hydrothermal-mechanochemical treatment of Eucalyptus enhances its enzymatic saccharification," *Bioresource Technology*, vol. 153, pp. 322-326, 2014.
- [33] L. Huang, B. Chen, M. Pistozzi, Z. Wu, and J. Wang, "Inoculation and alkali coeffect in volatile fatty acids production and microbial community shift in the anaerobic fermentation of waste activated sludge," *Bioresource Technology*, vol. 153, pp. 87-94, 2014.
- [34] C.-H. Weng, Y.-T. Lin, D.-Y. Hong, Y. C. Sharma, S.-C. Chen, and K. Tripathi, "Effective removal of copper ions from aqueous solution using base treated black tea waste," *Ecological Engineering*, vol. 67, pp. 127-133, 2014.
- [35] K. J. Sun, J. C. Tang, Y. Y. Gong, and H. R. Zhang, "Characterization of potassium hydroxide (KOH) modified hydrochars from different feedstocks for enhanced removal of heavy metals from water," *Environmental Science and Pollution Research*, vol. 22, no. 21, pp. 16640-16651, 2015.
- [36] V. B. H. Dang, H. D. Doan, T. Dang-Vu, and A. Lohi, "Equilibrium and kinetics of biosorption of cadmium(II) and copper(II) ions by wheat straw," *Bioresource Technology*, vol. 100, no. 1, pp. 211-219, 2009.
- [37] R. Han, L. Zhang, C. Song, M. Zhang, H. Zhu, and L. Zhang, "Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode," *Carbohydrate Polymers*, vol. 79, no. 4, pp. 1140-1149, 2010.
- [38] D. N. Barman, M. A. Haque, T. H. Kang et al., "Effect of mild alkali pretreatment on structural changes of reed (*Phragmites communis* Trinius) straw," *Environmental Technology*, vol. 35, no. 2, pp. 232-241, 2014.
- [39] M. Gorgievski, D. Božić, V. Stanković, N. Štrbac, and S. Šerbula, "Kinetics, equilibrium and mechanism of Cu²⁺, Ni²⁺ and Zn²⁺ ions biosorption using wheat straw," *Ecological Engineering*, vol. 58, pp. 113-122, 2013.
- [40] E. Espada-Bellido, M. D. Galindo-Riaño, M. García-Vargas, and R. Narayanaswamy, "Selective chemosensor for copper ions based on fluorescence quenching of a schiff-base fluorophore," *Applied Spectroscopy*, vol. 64, no. 7, pp. 727-732, 2010.
- [41] H. D. Peng, H. Z. Chen, Y. S. Qu, H. Q. Li, and J. Xu, "Bioconversion of different sizes of microcrystalline cellulose pretreatment by microwave irradiation with/without NaOH," *Applied Energy*, vol. 117, pp. 142-148, 2014.
- [42] R. Han, P. Han, Z. Cai, Z. Zhao, and M. Tang, "Kinetics and isotherms of Neutral Red adsorption on peanut husk," *Journal of Environmental Sciences*, vol. 20, no. 9, pp. 1035-1041, 2008.
- [43] R. Ebrahimi, A. Maleki, B. Shahmoradi et al., "Elimination of arsenic contamination from water using chemically modified wheat straw," *Desalination and Water Treatment*, vol. 51, no. 10-12, pp. 2306-2316, 2013.
- [44] B. Nagy, C. Mânzatu, A. Măicăneanu, C. Indolean, L. Silaghi-Dumitrescu, and C. Majdik, "Effect of alkaline and oxidative treatment on sawdust capacity to remove Cd(II) from aqueous solutions: FTIR and AFM study," *Journal of Wood Chemistry and Technology*, vol. 34, no. 4, pp. 301-311, 2014.
- [45] M. T. Ghaneian, G. Ghanizadeh, M. T. H. Alizadeh, M. H. Ehrampoush, and F. M. Said, "Equilibrium and kinetics of phosphorous adsorption onto bone charcoal from aqueous solution," *Environmental Technology*, vol. 35, no. 7, pp. 882-890, 2014.
- [46] S. M. Musyoka, H. Mittal, S. B. Mishra, and J. C. Ngila, "Effect of functionalization on the adsorption capacity of cellulose for the removal of methyl violet," *International Journal of Biological Macromolecules*, vol. 65, pp. 389-397, 2014.
- [47] H. Serencam, D. Ozdes, C. Duran, and H. B. Senturk, "Assessment of kinetics, thermodynamics, and equilibrium parameters of Cu(II) adsorption onto Rosa canina seeds," *Desalination and Water Treatment*, vol. 52, no. 16-18, pp. 3226-3236, 2014.
- [48] T. Y. Zheng, X. J. Yang, J. Song, and Y. L. Yang, "Investigation on the adsorption properties of Cu (II) in mine drainage by modified wheat straw," *Minerals Engineering*, vol. 9, pp. 57-60, 2011.
- [49] M. Makeswari and T. Santhi, "Use of *Ricinus communis* leaves as a low-cost adsorbent for removal of Cu(II) ions from aqueous solution," *Research on Chemical Intermediates*, vol. 40, no. 3, pp. 1157-1177, 2014.

