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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Removal of Metal Ions with Rice Husk-Based Sorbents

I. V. Sheveleva, A. N. Kholomeidik, A. V. Voit, N. P. Morgun, and L. A. Zemnukhova

Institute of Chemistry, Far East Branch, Russian Academy of Sciences, Vladivostok, Russia
Far East State University, Vladivostok, Russia

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Abstract—Sorption of metal ions from solutions of individual salts and their mixtures by rice husk-based sorbents was studied. The sorption properties of the rice husk were examined in relation to its modification conditions.

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As known, transition metal ions belong to most hazardous ecotoxicants adversely affecting the environment and human health.

Removal of transition metal ions from wastewater before discharging into water bodies, as well as in water treatment applications, still remains a problem to be solved in the optimal way. Today, heavy metal ions are most often removed from wastewater by chemical methods, specifically, precipitated as poorly soluble compounds to be further isolated.

Efficient treatment can be achieved with sorption methods in which the residual concentrations of different pollutants in water do not exceed in some cases the maximum permissible concentrations [1]. Heavy metal ions can be removed by sorbents based on both synthetic and natural materials: various fibrous sorbents [2], modified and technical lignins [3], gelatin-immobilized complexes of heavy metals [4], clays [5], silica gels [6], and modified granulated carbon adsorbents [7]. There has recently been increasing interest in natural sorbents. Raw material for them can be found in wood-processing wastes: chips, lignin, bark [3, 8], cellulose [9], and food-processing waste: chitin-containing materials yielded by integrated processing of biogenic raw materials (krill, shrimp, crab) [10], as well as in pits and integuments (soybean meal [11], husks, shells, and hulls of agricultural crops [12–14]).

Deoiled rice bran can be used for removal of chromium, copper, and zinc ions [13], and rice husk, of strontium, cadmium, nickel, lead, zinc, chromium, cobalt, and aluminum ions from solutions. Thus, rice manufacturing waste products as such are suitable as low-cost sorbents for treating various liquid media. Also, rice husk can be used for preparing carbonaceous, siliceous, or phosphorous materials with high sorption characteristics [15, 16].

Here, we elucidated the suitability of rice husk processing products as sorbents for removing Fe(III), Cu(II), Cd(II), and Pb(II) ions from aqueous solutions.

EXPERIMENTAL

As sorbents we used untreated rice husk (particle size no less than 2 mm) collected in Primorsk and Krasnodar krais, which was rinsed with water and dried at 105°C (sample no. 1), and the rice husk processing products (sample nos. 2–4) prepared by the schemes described in [16, 17] (Table 1). The samples prepared by acid and alkaline hydrolysis of the initial rice husk were thoroughly rinsed with distilled water till neutral pH was reached.

The content of silicon in the samples was determined gravimetrically [18], and that of carbon, by the procedure described in [19]. The specific surface area S_{sp}, $m^2\ g^{-1}$, of the sorbent was estimated by the standard technique [20] with Methylene Blue (Table 1).

Sorption was carried out under static conditions from $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 2H_2O$, $PbCl_2$ and $FeCl_3 \cdot 6H_2O$ (all analytically pure-grade) solutions with metals concentrations within 5–300 mg l^{-1}. The changes in pH of the solutions, specifically, from 5.73 to 5.55 for Cu(II), from 6.02 to 5.95 for Cd(II), from 6.10 to 5.65 for Pb(II),

and from 4.35 to 3.00 for Fe(III), depending on the metal concentration, were associated with hydrolysis of the salts solely. The sorbent was kept in the salt solutions for 24 h. Additional experiments showed that this time is sufficient for establishment of equilibrium. Similar data were reported by Srivastava et al. [14].

The metal concentration in solution was determined by atomic absorption spectroscopy on an AA-770 (Nippon Jarrell Ash) spectrophotometer in the acetylene–air flame.

The amount of the metal sorbed a, mg g^{-1}, was calculated by the formula

$$a = \frac{(c_{in} - c_{eq})V}{m\ 1000},$$

where c_{in} and c_{eq} are the initial and equilibrium concentrations, mg l^{-1}; V, volume of solution, ml; and m, weight of the weighed portion of adsorbent, g.

The removal α, %, of the metal ions was calculated by the formula

$$\alpha = \frac{c_{in} - c_{eq}}{c_{in}} \times 100.$$

To determine the parameters describing the sorption properties of the initial and modified rice husk, we obtained the isotherms of sorption of Fe(III), Cu(II), Cd(II), and Pb(II) ions from aqueous solutions of the corresponding salts (Figs. 1–4). The experimental data were described by the Langmuir equation for the sorption isotherm

$$a = \frac{a_{max} K_l c}{(K_l c + 1)},$$

where a is the sorption capacity, mg g^{-1}; a_{max}, maximal sorption capacity, mg g^{-1}; K_l, adsorption constant, l mg^{-1};

Table 1. Characterization and conditions of preparation of the sorbents

Sample no.	Conditions of preparation	S_{sp}, m^2 g^{-1}	Content, %	
			SiO_2	C
1	Rice husk	170	12.0	81.0
2	Rice husk after acid hydrolysis with 0.1 M HCl (90°C, 1 h)	196	15.0	72.0
3	Silica prepared from rice husk by the scheme: acid hydrolysis, two-step oxidative annealing (300 and 600°C) [16, 17]	295	99.0	0.001
4	Rice husk after alkaline hydrolysis with 1 M NaOH (90°C, 1 h)	200	0.05	83.0

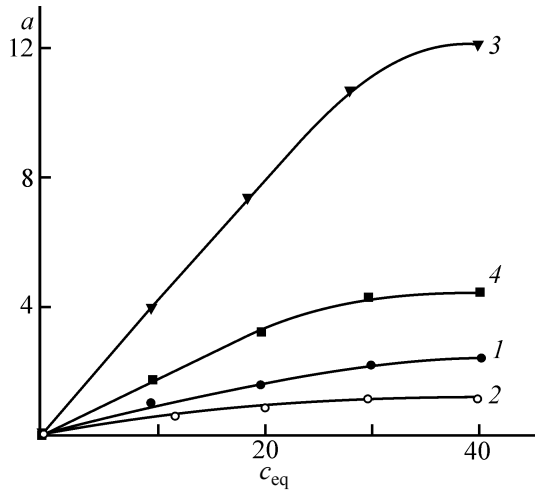

Fig. 1. Isotherms of Fe(III) ion sorption with rice husk-based sorbents. (a) Sorption capacity, mg g^{-1}; (c_{eq}) equilibrium concentration, mg ml^{-1}; the same for Figs. 2–4. Curve nos. correspond to the sample nos. in Table 1; the same for Figs. *2–4*.

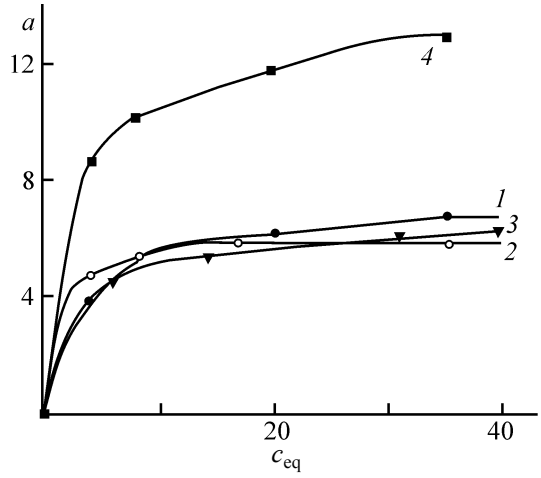

Fig. 2. Isotherms of Cu(II) ion sorption with rice husk-based sorbents.

and c, equilibrium concentration, mg l^{-1}.

Based on approximation of the sorption isotherms by the Langmuir equation we estimated the maximal sorption capacity a_{max} of the modified and initial rice husk with respect to Fe(III), Cu(II), Cd(II), and Pb(II) ions. The results of approximation are presented in Table 2.

Comparison of the data shows that the absorption capacity of the sorbents is strongly dependent on their preparation conditions. For example, acid hydrolysis of rice husk (sample no. 2) not only does not improve the sorption properties of the initial material (sample no. 1) but even decreases the capacity of the material with respect to iron(III) and cadmium(II). This can be associated with the earlier established fact [21] that acid hydrolysis of rice husk causes washing out of up to 13% water-soluble substances, including polysaccharides. The latter can contain functional groups (e.g., –OH, –COOH) participating in metal ion sorption.

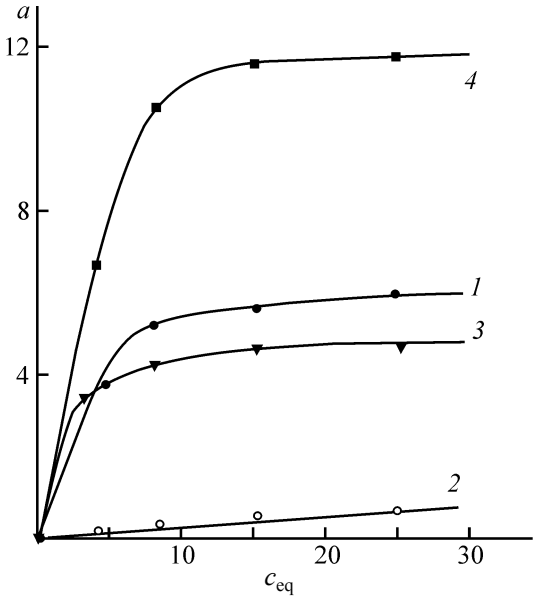

Fig. 3. Isotherms of Cd(II) ion sorption with rice husk-based sorbents.

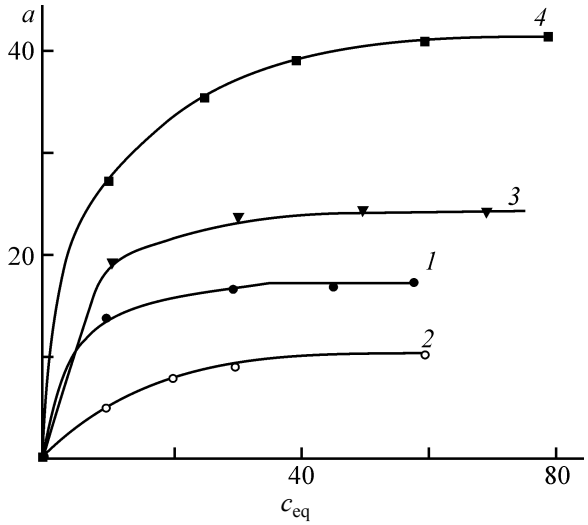

Fig. 4. Isotherms of Pb(II) ion sorption with rice husk-based sorbents.

Heat treatment of the rice husk after acid hydrolysis (sample no. 2) substantially modifies the structure of the new product (sample no. 3), specifically, causes its specific surface area to increase more than 1.5 times relative to the initial rice husk. The composition of the resulting sorbent is totally modified into essentially neat silicon dioxide (Table 1). This sorbent surpasses sample no. 2 in sorption capacity with respect to all the metal ions examined, and for iron(III) this is the most efficient sorbent among all the samples. Table 2 and Fig. 3 show that the sorption capacity of sample no. 3 with respect to cadmium(II) is lower than that of sample no. 1, though higher than that of the siliceous sample described by Srivastava et al. [14]. The reason is the difference in the preparation conditions and chemical compositions between sample no. 3 and the sorbent described in [14].

Alkaline hydrolysis of the rice husk improves the sorption properties of the initial material, and the resulting sorbent (sample no. 4) proved to be the most efficient in removing copper, cadmium, and lead ions. The sorption capacity of this sorbent strongly exceeds that of the initial rice husk, as well as those of sample nos. 2 and 3, which is associated with the difference in their compositions (Table 1). Indeed, Zemnukhova et al. [21] showed that, upon alkaline treatment of the initial rice husk, up to 52% water-soluble substances is removed. The insoluble plant carbon residue, free from silicon dioxide (Table 1), is able of swelling in an aqueous solution [22]. As a result, sorption can proceed not only on the surface but also in

Table 2. Maximal sorption a_{max} of the rice husk-based sorbents

Sample no. (according to Table 1)	a_{max}, mg g^{-1}			
	Fe(III)	Cu(II)	Cd(II)	Pb(II)
1	4.66	6.76	7.09	20.14
2	1.72	6.08	3.56	18.08
3	19.01	6.13	4.97	27.06
4	7.64	12.48	14.50	44.94

the bulk of the material. Moreover, the metal ion sorption on the sorbent (sample no. 4) proceeds presumably via complexing as well, since alkaline hydrolysis of plant raw materials causes the active functional groups (–OH, –O–, –CO, –COOH) to increase in number [23]. The sorbent prepared by Marshall et al. [13] via treating rice husk with 5% alkali solution exhibited a much lower sorption capacity with respect to copper(II) ions than does sample no. 4 [2.9 against 12.48 (Table 2) mg g^{-1}]. This difference in the sorption capacities can be associated not only with the conditions of preparation of the sorbents (the alkali treatment temperature for husk was not specified in [13]), but also with the properties of the initial rice husk used as precursor for the sorbent, which vary with the plant species.

Thus, comparative analysis of the absorption capacities of the examined sorbents showed that the best performance in removal of copper, cadmium, and lead ions is exhibited by sample no. 4 prepared by alkaline treatment of the rice husk. At the same time, sample no. 3 prepared by acid hydrolysis followed by two-step heat treatment is the best sorbent for iron. This sorption selectivity with respect to metal ions is evidently associated not only with the different compositions, structures, and surface properties of the sorbents (whose selected characteristics were examined by Zemnukhova et al. [24]), but also with the different forms of occurrence of these metals in solution depending on pH of solution [25].

Considering the fact that all aqueous media are essentially multicomponent solutions of various metal salts, it was of interest to study metal ion sorption from a mixture of components. We examined the absorption capacity of sorbent no. 4 with respect to Cu(II), Cd(II), and Pb(II) ions whose concentrations in mixed solutions was higher than those in single-component solutions and varied within 40–100 mg l^{-1}. The results (Fig. 5) suggest that 50% copper and lead is removed, while cadmium remains in solution. Thus, the sorbent prepared by alkaline hydrolysis of rice husk is suitable for separation of lead and copper from cadmium in solutions.

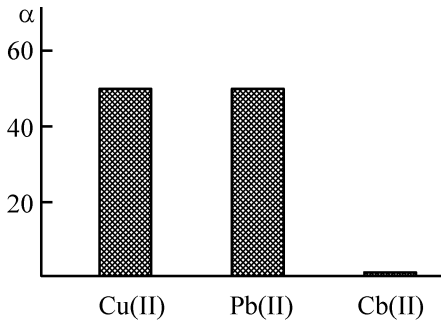

Fig. 5. Removal α, %, of copper, cadmium, and lead ions with sorbent no. 4 from mixed solution.

CONCLUSIONS

(1) Study of Fe(III), Cu(II), Cd(II), and Pb(II) ion sorption from individual solutions by rice husk-based sorbents showed that the sorption capacity of the sorbents depends on their preparation procedure. The highest sorption capacity with respect to Cu(II), Cd(II), and Pb(II) ions is exhibited by the sorbent prepared via alkaline hydrolysis of the rice husk, and with respect to Fe(III) ions, that prepared via heat treatment of the residue from acid hydrolysis of the husk, which is essentially amorphous silicon dioxide.

(2) The sorbent prepared by alkaline hydrolysis of the rice husk can be recommended for separation of lead and copper ions from cadmium ions in mixed solutions.

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