Removal of Cr^{3+} Ions by Phytic Acid Derivatives from Rice Bran

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The process of removing chromium(III) ions from aqueous solutions was investigated with respect to a phosphorus-containing product containing inositol hexaphosphoric acid derivatives obtained from rice bran-rice waste products of Far Eastern breeding varieties. The removal efficiency of chromium(III) ions by phosphorus-containing product depended on their initial concentration and reached 82%. Thus, environmentally friendly polyfunctional chelate materials from rice production wastes could be used to remove metal ions from aqueous solutions.

Keywords: Rice production wastes; Rice bran; Phytic acid; Removal of Cr(III)

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INTRODUCTION

Chromium and its compounds are widely used in the metalworking, leather, textile, chemical, paintwork, ceramic, match, and pyrotechnic industries (Mamyrbaev 2012). For example, in Russia there are approximately 7,000 individual electroplating plants that utilize chromium (Kolesnikov and Ilyin 2004). Output, processing, and any production associated with the use of chromium compounds is accompanied by its loss. Thus, industries using chromium compounds (III, VI) can have a negative impact on the natural environment, including the hydrosphere, due to the high toxicity of chromium compounds (Piotrowska *et al.* 2018). In Russia, chromium compounds are normalized in household water bodies (Cr(III): 0.5 $mg \cdot L^{-1}$, Cr(VI): 0.05 $mg \cdot L^{-1}$ (GN 2.1.5.1315-03 2003)) and fishery productions (Cr(III): 0.07 $mg \cdot L^{-1}$, Cr(VI): 0.02 $mg \cdot L^{-1}$ (Ministry of Agriculture of the Russian Federation 2016)). The maximum permissible concentration of Cr(III) in drinking water is 0.05 $mg \cdot L^{-1}$; Cr(VI) is not standardized (SanPiN 2.1.4.1074-01 2001).

Various artificial and natural porous materials having developed specific surface area are used to remove cations of toxic metal from aquatic media, including zeolites (Aljerf 2018), carbon-containing terpels (Shashkova *et al.* 2001), dolomites (Sdiri 2018), and carbon sorbents based on vegetable and animal raw materials (Pakshirajan *et al.* 2013; Elabbas *et al.* 2015). When treating wastewater containing heavy metal ions, the main practical task is to select local materials that are of a low cost but effective. Agricultural wastes that accumulate in large quantities every year are of a practical interest as raw and inexpensive materials that can be used for wastewater treatment.

In 2016–2017, rice production increased to 482 million tons according to the estimates of the International Grain Council (2017). Consequently, the formation of a large-tonnage of by-products in the form of rice husk and bran, which are concentrated on groats mills and requiring disposal, has increased. The main advantages of such raw material are its annual reproducibility, low cost, and almost constant chemical composition for a single plant species and a growing region (Sergienko *et al.* 2004).

One of the products obtained from rice production waste (rice bran) is inositol hexaphosphoric acid (IHPA, phytic acid) and its derivatives (phytin) (Greiner and Konietzny 2006). Phytic acid and its salts are highly efficient ligands that chelate metal cations, which allows them to be used to remove heavy metal ions from aqueous solutions (Sidorova, 2015). The process of removing cobalt, nickel, and aluminum ions from aqueous solutions with phosphorus-containing product obtained from rice bran has been studied in the Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences (Kovekhova *et al*. 2018; Yarusova *et al*. 2018).

The purpose of this work was to study the conditions for chromium(III) removal from aqueous solutions by phytic acid derivatives extracted from rice bran.

EXPERIMENTAL

Phosphorus-containing products were obtained from rice bran of the Far Eastern breeding rice varieties using a published method (Kolzunova *et al.* 2000).

The Choice of the Ratio S:V (Sample Weight: Solution Volume)

The ratio of the sample mass to the volume of the solution was selected as follows. Chromium chloride solution was prepared by dissolving an exact weight in distilled water. The measured concentration of Cr^{3+} was 8.1 $mg \cdot L^{-1}$. Next, 25 mL of an aqueous solution of salt and a portion of a phosphorus-containing product weighing 0.017, 0.025, 0.050, 0.10, 0.25, and 0.50 g were placed into conical flasks with a volume of 50 mL, which corresponded to the mass ratio of the sample to the volume of solution (S: V) 1: 1500, 1: 1000, 1: 500, 1: 250, 1: 100, and 1: 50, respectively. The flasks were closed with stoppers, and the contents were stirred at room temperature on a Unimax 1010 device (Heidolph, Germany). After 60 min the solution was separated from the sample by filtration. The residual Cr^{3+} content in the filtrate was determined by atomic absorption spectrometry on a SOLAAR M6 two-beam spectrometer (Thermo Scientific, Waltham, MA, USA) using analytical lines of 240.7, 460.7, 283.3, 228.8, 213.9, 232.0, 324.8, and 279.5 nm. The result was the average of the results of three parallel measurements.

Elemental composition of the phosphorus-containing product before and after the removal of chromium ions was determined by the semi-quantitative method of energy dispersive X-ray fluorescence spectroscopy (ED XRFS) on an EDX 800 HS spectrometer (Shimadzu, Kyoto, Japan). A tablet (radiator) with a diameter of 20 mm was pressed from the test sample, and the spectra of elements of 100 s were measured in each energy channel. The radiating source was a tube with an Rh - anode. The concentration of elements was calculated by the method of fundamental parameters using software spectrometer without light elements.

Removal of Chromium Ions from Aqueous Solutions Over Time

First, 25 mL of a chromium chloride solution (Cr^{3+}, 8.1 $mg \cdot L^{-1}$) were added into a 50 mL conical flask. The mass of the phosphorus-containing product when extracting chromium ions was 0.1 g. The flasks were closed with stoppers, and the contents were stirred at 25 °C on a Unimax 1010 device. After 30, 60, 90, 180, and 360 min, the solution was filtered, and the residual Cr^{3+} content was determined in the filtrate. The arithmetic average of the results of three parallel determinations was taken as the result. The removal of chromium ions (ɳ, %) was calculated by Eq. 1,

$$\eta\,(\%) = \frac{C_{in} - C_{eq}}{C_{in}} \times 100 \qquad (1)$$

where C_{in} and C_{eq} are the initial and the equilibrium concentrations of chromium ions ($\text{mg}\cdot\text{L}^{-1}$), respectively. A kinetic curve was plotted to show the removal of chromium ions *vs*. time.

Removal of Chromium Ions from Aqueous Solutions Depending on their Initial Concentration

The study of the removal of chromium ions was carried out at a ratio S: V = 1: 250. For this test, 25 mL of a Cr^{3+} solution with measured concentrations of 2.26, 7.90, 14.76, 20.20, 28.20, 56.60, and 70.70 $\text{mg}\cdot\text{L}^{-1}$ was placed into 50 mL conical flasks. The flasks were shaken for 60 min. After mixing, the suspension was filtered, and the residual content of chromium ions was determined. The average of three parallel determinations was used as the result. The removal of chromium ions from aqueous solutions (ɳ, %) was calculated using Eq. 1, and the dependence of the initial concentration was plotted.

pH in an Aqueous Phytin Suspension in a Solution of Cr (III) Over Time

The pH of various media was measured on a pH meter (SevenCompact, Mettler Toledo, Zurich, Switzerland) using X-Lab software. First, 50 mL of an aqueous solution of chromium chloride (Cr^{3+}, 70.70 $\text{mg}\cdot\text{L}^{-1}$) were placed in the potentiometric cell. The glass electrode was placed in the solution, and after the potential was stabilized, 0.1 g of phosphorus-containing product was added. The pH value was measured during 60 min with constant stirring.

RESULTS AND DISCUSSION

The dependence of chromium removal degree at different ratios of S: V is shown in Fig. 1. With S:V ratios from 1:1500 to 1:250, the chromium removal rate increased from 50 to 73%. When the ratio dropped to 1:100 and 1:50, it increased by 6 to 7%. Therefore, further studies of the removal of Cr^{3+} ions were conducted with an S: V ratio of 1:250.

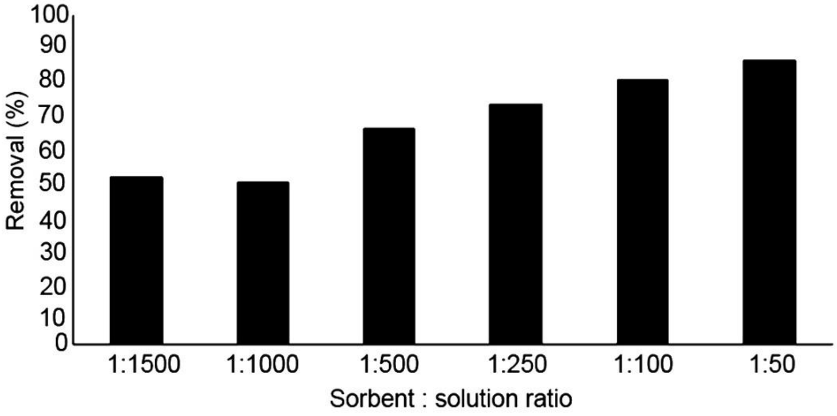

Fig. 1. The degree of removal of chromium ions at different ratios of S: V

Plotting the removal degree *versus* time (Fig. 2) showed that 73% of the chromium ions were extracted from aqueous solutions after 60 min, after which the rate slowed, reaching the maximum level of 82% after 6 h. Based on this data, the duration of the experiment was set at 60 min.

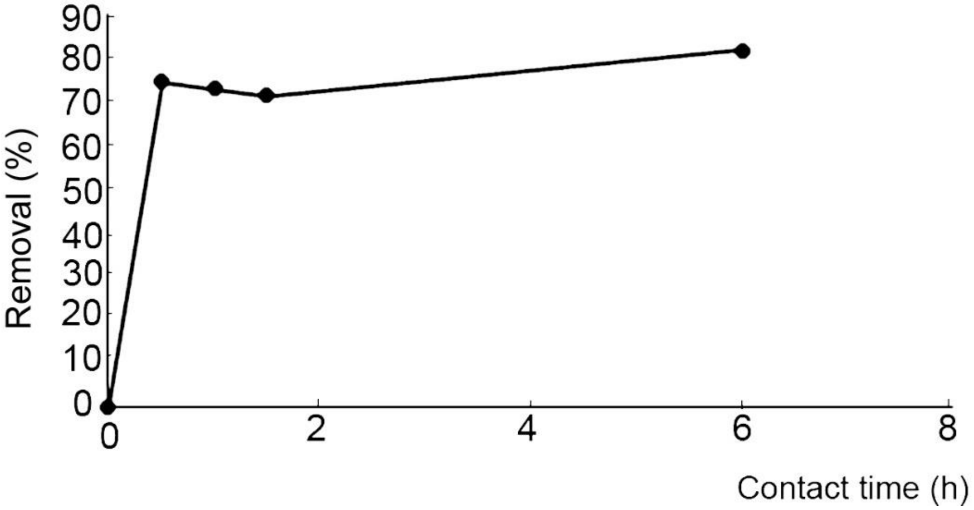

Fig. 2. Kinetic curve of the change in the removal of chromium ions from aqueous solutions of phosphorus-containing product from rice bran

In the process of removing chromium ions from an aqueous solution (Cr^{3+}, 70.70 mg·L^{-1}), the pH of the medium changed from 3.2 to 6.0 (Fig. 3). At the beginning of the experiment, the pH of the medium gradually increased and stabilized after 15 min in the range of 5.8 to 6.0. An increase in the pH value of the solution occurred apparently, due to the binding of the chromium cation with the derivatives of IHPA.

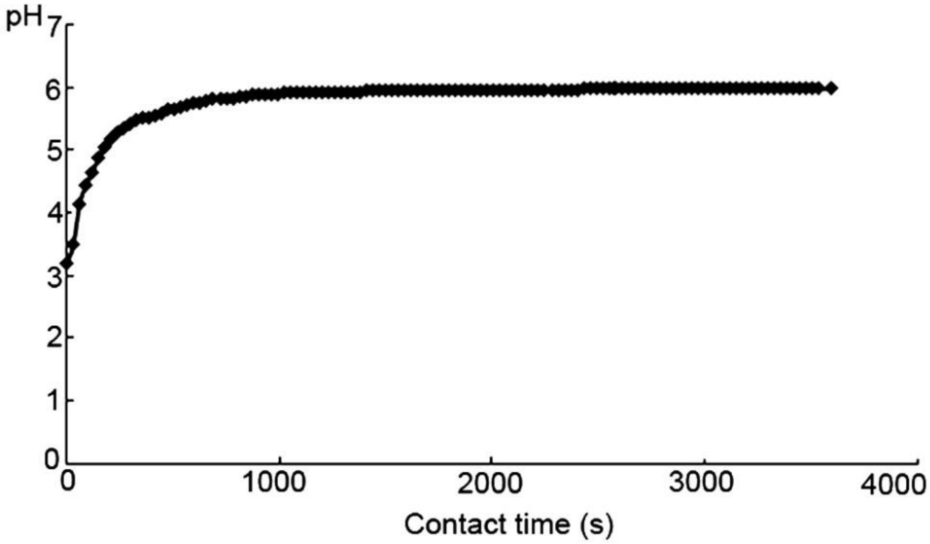

Fig. 3. Changes in the pH during the removal of Cr^{3+} ions from aqueous solutions

As shown in Fig. 4, the removal of chromium ions from solutions with a phosphorus-containing product increased with increasing Cr^{3+} concentration from 40% to 92%. This result might be due to the increase in phytin solubility with increasing pH of the solution. As shown in Makarenko *et al.* (2018), the phytin solubility at pH 3 is 0.239 g/100 g water, while at pH 5 it is 0.189 g/100 g. The result indicates that the removal of chromium(III) occurs due to interaction of chromium ions and phytin in solution with the formation of insoluble compounds.

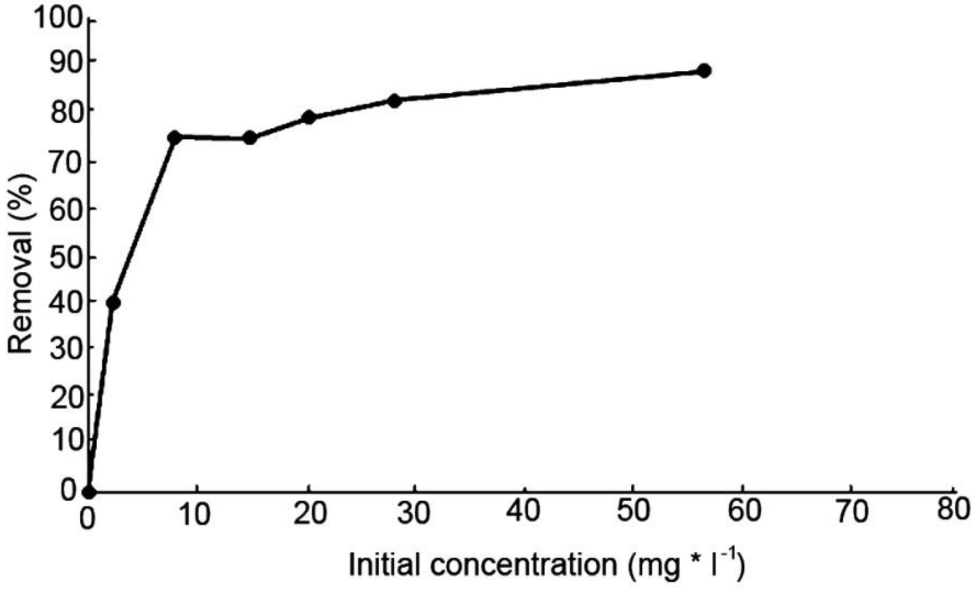

Fig. 4. The removal of Cr^{3+} ions from aqueous solutions depending on their initial concentration

The change in the pH of the medium during chromium ion removal from depended on the initial concentration of the solute (Table 1). After removal, the pH of the medium increased approximately 2 pH units.

Table 1. pH Values During the Removal of Chromium Ions from Solutions

Initial Concentration (mg·L^{-1})	pH Before Removal	pH After Removal	ΔpH
2.26	5.2	6.8	1.6
7.90	4.5	6.1	1.6
14.76	4.1	5.9	1.8
20.20	4.0	5.7	1.7
28.20	3.7	6.0	2.3
56.60	4.0	5.5	1.5
70.70	3.2	5.6	2.4

The phosphorus-containing product before and after contact with the solution of chromium salt was studied by energy dispersive X-ray fluorescence spectroscopy. In the sample, after the removal of Cr^{3+} ions from a solution with the concentration of 70.70 mg·L^{-1}, the presence of chromium in the amount of 20 % was registered (Table 2).

An increase in the pH value of the medium and the appearance of chromium in the sediment after contact of the model solution with the phosphorus-containing product confirmed the removal of Cr^{3+} ions.

Table 2. Elemental Composition of the Phosphorus-containing Product Before and After the Removal of Chromium Ions

Element	Content (%)	
	Before Cr^3 Extraction $^+$	After Cr^{3+} Extraction
P	45	53
Cr	-*	20
Mg	26	18
K	12	4
Ca	4	2
Mn	2	2
*- the parameter was not identified		

CONCLUSIONS

1. The present work shows the possibility of using phosphorus-containing product from rice bran to remove Cr^{3+} ions from aqueous solutions in the concentration range from 2 to 70 $mg\cdot L^{-1}$ in the pH range from 5 to 3 (t=25 ºC).
2. The obtained results offer a fundamental possibility of using environmentally friendly polyfunctional chelate materials from rice production wastes to remove metal ions from aqueous solutions.

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