OBTAINING COAGULANT FROM AUMINZATAU KAOLIN FOR PPM WASTEWATER PURIFICATION

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ABSTRACT

This article is devoted to the development of methods for obtaining raw materials and coagulants based on Auminzatau kaolin at the Zarkuduk site and the treatment of highly coloured wastewater from the production of paper from rice and wheat straw. The yield of kaolin, treated with a 30 % hydrochloric acid solution at an optimum calcination temperature of 500°C for 90 min, was 97.5 %. The optimum temperature for the interaction of hydrochloric acid is 25 - 30°C for 30 - 45 min. The efficiency of the coagulant application is 97.5 %.

Keywords: kaolin, hydrochloric acid, calcination, alumina, iron oxide, leaching, coagulant, coagulation, cooking water, wastewater, purification, treatment pond.

INTRODUCTION

Existing technology development for obtaining reagents and wastewater treatment methods with their use, pursuing the goal of returning purified water and extracting valuable components to the enterprise, is an urgent problem of modern industries such as oil and paper.

In many countries of the world, research work is underway to obtain coagulants for the treatment of industrial-coloured wastewater from paper products based on natural or synthetic raw materials. Among the most common raw materials for getting coagulants are kaolin and kaolin clays, which have sorption properties [1]. The deterioration of the ecology of clean watercourses during the diversion of polluted industrial waters, along with impurities and substances useful for production, dictates the need to extract such materials and improve the degree of their purity of water from harmful pollutants. Therefore, research is underway to develop methods for treating wastewater, obtaining purified water suitable for the needs of industries, and meeting the requirements of approximately safe levels of harmful substances [2].

Kaolinites (38 - 43 %) and bauxites (40 - 70 %) rich in aluminium oxide are found in Europe, in watered regions of Russia, and in the countries of Oceania (Malaysia, Indonesia, etc.) [3 - 6]. In the crystal lattices of kaolinite, the bond length between the packages of crystals practically does not change and is described by the chemical formula $2[Al_2Si_2O_5](OH)_4$ [4].

Primary kaolin contains 45 - 60 % quartz, and secondary ones are mainly kaolin clays with a high content of alumina [7].

There is a wide range of kaolin deposits, containing a sufficient amount of alumina with various amounts of iron oxides, in Uzbekistan.

The Angren kaolin coal deposit is unique among all coal deposits known in Central Asia. From 1960 - 67 primary kaolin's were systematically explored in detail on the territory of open-pit coal mining to a depth of more than 250 m 11 % [8].

The Zarkuduk section of the Auminzatau kaolin deposit contains secondary kaolin's with a high content of Al_2O_3, which reaches 38 - 40 % [8].

There are works devoted to the kinetics of alumina extraction using various methods. In particular, the technique of thermochemical destruction of kaolin established an imperceptible degree of aluminium oxide extraction at sintering temperatures of 300 - 400°C. An increase in the sintering temperature to 500 °C contributes to the increase in the degree of Al_2O_3 extraction, and at 600 - 700°C, the degree of extraction of aluminium oxide reaches a maximum value of 92 - 95 % [9, 10]. Up to 850°C, the degree of extraction of aluminium oxide into the solution increases sharply and reaches 92 %. With an increase in the firing temperature from 850°C to 900°C, the extraction of alumina into the solution noticeably decreases [11].

The study aims to develop a method for obtaining raw materials and coagulants based on Auminzatau kaolin at the Zarkuduk site and for treating highly coloured wastewater from paper and wheat, and rice straw production.

This article first presents the results of studies on the effect of heat, and calcination time on the extraction of aluminium oxide from kaolin Auminzatau of the Zarkuduk site, to obtain coagulants from it. Zarkuduk kaolin is of interest due to the high content of aluminium oxide and the smallest amount of iron oxide [12 - 15].

Kaolin "Extra" unenriched, extracted from the Zarkuduk section of the Auminzatau deposit, has a chemical composition (wt.%): Al_2O_3 - 35.00, Fe_2O_3 - 1.05, SiO_2 - 52.69, TiO_2 - 0.36, CaO - 0.45, MgO - 0.31, $K_2O + Na_2O$ - 1.44, p.p.p.- 8.70.

Before calcination, kaolin was treated with a 30 % hydrochloric acid solution and then subjected to calcination in the temperature range of 20 - 600°C. At the 20 - 280°C temperature, no significant changes in the decomposition of kaolin into its constituent parts were observed.

Starting from a temperature of 300°C, the decomposition of kaolin was clearly observed. After leaching the decomposed kaolin with a 3 % hydrochloric acid solution and heat treatment at 105 - 110°C for 30 - 45 min, followed by operations to remove impurities, the mass of the resulting raw material was determined to obtain a coagulant.

Table 1 shows the influence of the calcination temperature of kaolin on the degree of aluminium oxide extraction from it.

Table 1 shows that an increase in the kaolin calcination temperature to 500°C and the calcination

Table 1. Influence of temperature and duration of calcination on the degree of extraction of aluminium and iron oxides from unenriched kaolin's (sample -1000 g).

Kaolin type	Ignition temperature T, °C	Calcination time, min	Weight loss, %	Component recovery			
				Al_2O_3, G	Fe_2O_3, G	Al_2O_3, %	Fe_2O_3, %
unenriched	300	60	2.3	37.170	4.412	10.62	42.02
unenriched	300	90	2.8	77.455	4.642	22.13	44.21
unenriched	350	60	5.4	175.420	5.494	50.12	48.09
unenriched	350	90	6.4	214.831	5.547	61.38	52.83
unenriched	400	60	7.1	258.895	2.990	73.97	56.95
unenriched	400	90	7.6	281.260	3.417	80.36	65.08
unenriched	450	60	8.0	293.723	3.736	83.92	71.16
unenriched	450	90	8.8	297.998	3.768	85.14	74.77
unenriched	500	60	9.8	299.495	3.448	85.57	71.33
unenriched	500	90	9.6	300.304	3.335	85.80	63.52
unenriched	550	60	9.6	247.345	2.372	70.67	45.19
unenriched	600	60	9.6	161.315	2.304	46.09	43.88

time have a positive effect on the extraction of aluminium and iron oxides. A high degree of extraction of alumina from kaolin is achieved at a temperature of 500°C. A further increasing temperature probably leads to the formation of aluminium and iron silicates.

It is likely that at such a low temperature, the reaction between the oxides of aluminium, iron, and the residual amount of silicon possibly proceeds according to the equations:

$$Al_2O_3 + SiO_2 \xrightarrow{t > 500^oC} Al_2SiO_5;$$
$$Fe_2O_3 + SiO_2 \xrightarrow{t > 500^oC} Fe_2SiO_5;$$
$$FeO + SiO_2 \xrightarrow{t > 500^oC} FeSiO_3;$$
$$4Al + SiO_2 \xrightarrow{t > 500^oC} Al_4Si_{3+}O_2\uparrow;$$
$$4Fe + SiO_2 \xrightarrow{t > 500^oC} Fe_4Si_{3+}O_2\uparrow;$$
$$2Fe + SiO_2 \xrightarrow{t > 500^oC} Fe_2Si_{+}O_2\uparrow.$$

The repetition of the same indicators with enriched kaolin showed a significant increase in the yield of aluminium and iron oxides by more than 10 %.

The calcination time also initially positively affects the extraction of aluminum oxide from the kaolin of the Zarkuduk section of the Auminzatau tract. A sharp decrease is observed (Table 2).

From Table 2 it is easy to see a monotonous increase in the yield of aluminium oxide in the temperature range of 300 - 500°C and the calcination time. The optimal time for calcining Zarkuduk unenriched kaolin "Extra" is 60 min and for enriched kaolin 90 min.

Reaction equations before calcination of kaolin after treatment with a 30 % hydrochloric acid solution:

$$2SiO_2\cdot Al_2O_3 + 6HCl \rightarrow 2SiO_2\cdot 2AlCl_3 + 3H_2O;$$
$$2SiO_2\cdot Fe_2O_3 + 6HCl \rightarrow 2SiO_2\cdot 2FeCl_3 + 3H_2O;$$
$$2SiO_2\cdot TiO_2 + 4HCl \rightarrow 2SiO_2\cdot TiCl_4 + 2H_2O;$$
$$2SiO_2\cdot CaO + 2HCl \rightarrow 2SiO_2\cdot CaCl_2 + H_2O;$$
$$2SiO_2\cdot K_2O + 2HCl \rightarrow 2SiO_2\cdot 2KCl + H_2O;$$
$$2SiO_2\cdot Na_2O + 2HCl \rightarrow 2SiO_2\cdot 2NaCl + H_2O;$$

Reaction equations for kaolin treated with a 30 % hydrochloric acid solution after calcination:

$$2SiO_2\downarrow 2AlCl_3 + 3H_2O \xrightarrow{t = 400-450^oC} 2SiO_2\downarrow + Al_2O_3 + 6HCl;$$
$$2SiO_2\downarrow 2FeCl_3 + 3H_2O \xrightarrow{t = 400-450^oC} 2SiO_2\downarrow + Fe_2O_3 + 6HCl;$$
$$2SiO_2\downarrow\cdot TiCl_4 + 2H_2O \xrightarrow{t = 400-450^oC} 2SiO_2\downarrow + TiO_2 + 4HCl;$$
$$2SiO_2\downarrow\cdot CaCl_2 + H_2O \xrightarrow{t = 400-450^oC} 2SiO_2\downarrow + CaO + 2HCl;$$
$$2SiO_2\downarrow\cdot 2KCl + H_2O \xrightarrow{t = 400-450^oC} 2SiO_2\downarrow + K_2O + 2HCl;$$
$$2SiO_2\downarrow\cdot 2NaCl + H_2O \xrightarrow{t = 400-450^oC} 2SiO_2\downarrow + Na_2O + 2HCl.$$

Table 2. Temperature and calcination time effects on the yield of aluminium and iron oxides from enriched kaolin (1000 g of kaolin).

Kaolin type	Ignition temperature T, °C	Calcination time, min	Weight loss, %	Component recovery			
				Al_2O_3, g	Fe_2O_3, g	Al_2O_3, %	Fe_2O_3, %
enriched	300	60	2.3	57.876	2.206	13.22	42.02
enriched	300	90	2.8	122.850	2.321	28.05	44.21
enriched	350	60	5.4	258.166	2.525	58.96	48.09
enriched	350	90	6.4	296.088	2.7736	67.62	52.83
enriched	400	60	7.1	394.182	3.096	90.02	58.95
enriched	400	90	7.6	420.824	3.496	96.10	66.58
enriched	450	60	8.0	423.620	3.815	96.74	72.66
enriched	450	90	8.8	425.340	3.945	97.13	75.14
enriched	500	60	9.8	426.500	3.745	97.57	71.33
enriched	500	90	9.6	430.350	3.267	98.28	62.22
enriched	550	60	9.6	346.470	2.477	79.12	47.19
enriched	600	60	9.6	282.450	2.387	64.50	45.47

Treatment with a concentrated hydrochloric acid solution is necessary to weaken the bonds of the crystal lattice and the forces of the intermolecular setting. The attendance of polar hydrochloric acid molecules will primarily promote interaction with metal oxides and repel them from silicon dioxide (sand). Thus, the resulting water will further weaken the cohesive forces between the metal salts and the sand.

During calcination, salt hydrolysis occurs with the simultaneous displacement of water from the formed hydrochloric acid salts of metals. In this way, metal oxides are formed again, divided from the sand, and bound by van der Waals or adsorption forces of attraction.

The resulting clay mass is processed with a 3 % hydrochloric acid solution to transfer the metal salt into the solution. Insoluble silicon dioxide and other water-insoluble impurities precipitate out. The precipitate is filtered off, then the solution is heated to a temperature of 70 - 75°C, and finally, the formation of a precipitate is observed. The products of hydrolysis of hydrochloric acid salts precipitate, hydroxides of aluminium, and iron (III). The precipitate is separated, carefully washed with small portions of cold water, and dried. The resulting dry precipitate is crushed, weighed on a balance, and placed in a beaker 10 % hydrochloric acid solution is carefully added, constantly stirring with a glass rod until 5 - 5.5 pH. In this case, the precipitate will completely dissolve in water [15].

The optimal conditions for obtaining a coagulant from unenriched kaolin from the Zarkuduk area of the Zarkuduk tract are given in Table 3.

Cooking waters flowing into the treatment pond contain inorganic and organic substances, shown in Table 4. For their purification, 10 % solutions of the obtained coagulants were added (at 10 L per 1 m^3 rate of cooking water draining into the treatment pond) into the coloured wastewater of rice and wheat straw. The effluent of rice straw pulping was called SVRS, and the wheat straw pulping SVPS was abbreviated.

The addition of solutions of these coagulants made it possible to remove harmful elements barium, boron, tin, and strontium, as well as elements that form dyes - cobalt, manganese, nickel, from the composition of SVRS, to reduce the other elements' concentration and 4 classes of organic substances up to maximum permissible concentrations. The results of studies of the wastewater compositions before and after the treatment of highly coloured cooking waters show the data in Table 4.

Table 3. The optimal conditions for the coagulant obtaining process.

Indicators and unit of measurement	Values
Ignition temperature, °C	550 ± 10
Optimal calcination time, min	90
Cooling time, min	60
Cooling temperature	20 - 25
Acid treatment temperature, °C	97 ± 2
pH of the reaction medium	5 - 5.5
Reaction time, min	60
Filtration temperature, °C	25 - 30
Evaporation temperature, °C	97 ± 2
Evaporation time, min	150
Drying temperature, °C	110 ± 2
Drying time, min	60
Packaging temperature,	20
Packing time, min	60
Total cycle time, min	540

The return of valuable substances such as lignin, cellulose, polysaccharides, and organosilicon compounds is an integral part of the study. The applied coagulant formed slightly insoluble derivatives of organic substances that coagulated and precipitated. The precipitation had a flaky appearance.

The results of studying the changes in the composition of wastewater organic substances are shown in Table 5, where it is easy to notice the effect of coagulation hundreds of times. The return of such a quantity of valuable secondary raw materials to the enterprise for obtaining paper can serve science and economics as a significant contribution.

From Table 4 and 5, the wastewater from the rice and wheat straw cooking was heavily contaminated, and the coagulation treatment became colourless and transparent. The quality indicators of treated waters were as in Table 6.

A comparative analysis of the average values of wastewater quality indicators before and after treatment in Table 6 shows the effectiveness of the use of the coagulant, which consists in reducing: colour intensity by 14, colour by 1000, COD by 52, BOD by about 60 and water hardness by 20 times.

Table 4. Results of studies of highly coloured wastewater compositions before and after treatment.

Names of elements	Symbol	Contents in ash			
		Before cleaning		After cleaning	
		SVRS	SVPS	SVRS	SVPS
Aluminium	Al	17.6 ± 0.1000	3.5 ± 0.1000	1.47 ± 0.0100	3.5 ± 0.1000
Barium	Ba	0.17 ± 0.0100	-	-	-
Bor	B	0.06 ± 0.0050	0.011 ± 0.1000	-	0.001 ± 0.1000
Iron	Fe	0.36 ± 0.0200	3.6 ± 0.1000	0.03 ± 0.0200	3.6 ± 0.1000
Calcium	Ca	11.2 ± 0.1000	18.4 ± 0.1000	1.12 ± 0.0050	18.4 ± 0.1000
Cobalt	Co	0.035 ± 0.0010	-	-	-
Silicon	Si	18.1 ± 0.1000	9.4 ± 0.1000	1.31 ± 0.1000	9.4 ± 0.1000
Magnesium	Mg	3.6 ± 0.1000	5.9 ± 0.2000	0.32 ± 0.1000	5.9 ± 0.2000
Manganese	Mn	0.099 ± 0.001	0.112 ± 0.002	-	-
Copper	Cu	0.054 ± 0.001	0.011 ± 0.001	0.004 ± 0.0001	0.001 ± 0.0001
Molybdenum	Mo	0.002 ± 0.0002	0.007 ± 0.0005		
Sodium	Na	22.3 ± 0.0200	25.40 ± 0.2000	1.83 ± 0.0200	2.54 ± 0.0200
Nickel	Ni	0.009 ± 0.0001	0.006 ± 0.0005	-	-
Tin	Sn	0.001 ± 0.0001	0.018 ± 0.0020	-	0.01 ± 0.0010
Strontium	Sr	-	0.018 ± 0.001	-	-
Titanium	Ti	0.054 ± 0.001	0.38 ± 0.0050	0.004 ± 0.0001	0.028 ± 0.002

Table 5. Results of studying composition changes of organic substances in wastewater.

Name substances	Unit of measurement	Contents in wastewater			
		Before cleaning		After cleaning	
		SVRS	SVPS	SVRS	SVPS
Lignin	kg m^{-3}	12.1 ± 0.5	13.4 ± 0.6	0.06 ± 0.005	0.064 ± 0.006
Hemicellulose	kg m^{-3}	14.6 ± 0.4	16.4 ± 0.4	0.07 ± 0.003	0.074 ± 0.60
Polysaccharides	kg m^{-3}	3.6 ± 0.4	4.3 ± 0.4	0.02 ± 0.002	0.034 ± 0.003
Organosilicon substances	kg m^{-3}	3.4 ± 0.4	1.2 ± 0.6	0.012 ± 0.001	0.032 ± 0.006

Table 6. Average values of quality indicators of wastewater from the pulp and paper industry.

Water quality indicators	Limits of change	
	Before purifying	After purifying
Colour intensity	1:35 - 1:100	1:2.5
Ash content of dry residue, %	44 - 49	1.8 - 1.9
Waste water pH	6.8 - 8.80	6.84 - 7.22
Undissolved substances, mg L^{-1}	210 - 220	33 - 38
Dry residue, mg L^{-1}	1800 - 2900	55.00 - 81.20
Chemical need in oxygen (COD), mLO_2 L^{-1}	1730 - 1820	33.80 - 34.20
Biological need in oxygen (BOD), mLO_2 L^{-1}	310 - 800	8.42 - 8.51
Colour, degree	127000 ± 3000	127.00 ± 3.00
Hardness mg-eq L^{-1}	15.5 ± 0,2	0.75 ± 0.06

CONCLUSIONS

This article has discussed the possibility of obtaining a coagulant from kaolin by thermochemical extraction for the highly coloured wastewater treatment from paper production. Temperature effect on the recovery of aluminium and iron oxides has been studied.

It has been established that a high degree of extraction of alumina from kaolin is achieved at 500°C temperature. Raising temperature probably leads to the formation of aluminium and iron silicates. Coagulant application made it possible to remove barium, boron, tin, and strontium ions from the composition of wastewater, such as cobalt, manganese, and nickel ions that give colour to sewage.

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