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To cite this article: S L Fux *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **272** 022053

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Geosorbent Based on the Combination of Kuznetsk-Basin Coal Fly Ash With Various Kinds of Lignin

S L Fux¹, S V Devyaterikova¹, T A Musikhina¹

¹Vyatka State University, Moskovskaya street, 36, City of Kirov, 612100, Russia

E-mail: usr01730@vyatsu.ru

Abstract. Annually coal-fired heat-and-power plants produce up to 40 million tons of ash and slag in Russia, while the already accumulated in the ash-dumps waste exceeds 1.5 billion tons. In Russia alone heat power plants' ash-dumps occupy over 20 thousand km² of land area. Ash and slag waste reclamation volume in Russia doesn't exceed 6 % of of their annual accumulation (annually only 1.5-2.1 million tons are recycled), while other countries recycle 50-100 % of ash and slag waste. Russia's main coal-mining region is the Kuznetsk coal basin. The importance of the suggested fly ash geosorbent technology is in the fact that its use will make it possible to recycle and reclaim the already accumulated ash and slag waste, but the newly produced waste as well. Thus, the objective of the project in question is the study of the use of heat power plant fly ash as a gas-adsorbing agent in the chemical industry, and as a means to extract industrial oils and lubricants out of waste water.

1. Intrudaction

About 170 thermal power plants (TPP) in Russia burn coal as fuel. Such significant accumulation of solid waste in the power industry is the outcome of the existing technology of raw materials processing and inadequate use of ash and slag waste (ASW). Current level of ASW recycling is extremely low in Russia. As of 2012 the ASW recycling volume didn't exceed 6 % of annual accumulation, however, in the USA the ASW recycling volume is no less than 50% of annual accumulation, meanwhile in Germany the doctrine says: "A coal-burning power station, no ash dump". In the Scandinavian countries the CHP plant ash recycling has reached 100 %. Members of the European Coal Combustion Products Association consider coal ash as a valuable raw and building material. The Association was founded in 1990, and includes 28 power companies from 15 countries, accounting for 88% of EU ash and slag waste.

Ash and slag pollute the environment with dust and radioactive particles, heavy metals contaminating ground waters. Some spontaneous fires happen in case there is some underburnt coal dust in the ash. Hence, one the important issues regarding the technosphere issues is elimination of overfilled ash dumps by recycling the accumulated ash and slag waste into materials suitable for use in various industries. To effectively use such materials there is a need for new recycling technologies including the ones integrating lignin, for instance. Lignin is bulk waste resulting from wood hydrolysis in biochemistry.

The fly ash is known to be a valuable mineral residue left upon burning coal in boilers of thermal power plants. It is a multi-component product of geo-resources high-temperature combustion, and as such it can be recycled to serve as secondary material resource and be used to obtain a variety of



materials [1-20]. The fly ash constituents are used in liquids and gases purification adsorbents, which is a feasible solution of recycling the fly ash, a large-volume waste of thermal power plants. Fly ash is nothing else but a geopolymer demonstrating high binding properties so typical of low-calcium aluminosilicate systems. When devising the composition of the geopolymer binder one should take into account the following: the fly ash's composition and properties, the type of the burnt coal, the combustion method, the fire cone's temperature, the ash handling, collection and storage, tonnage, the percentage used, the cost estimates, the environmental impact, combustibility, etc.. Thus, to develop both new and understudied ways of ash utilization, it is also useful to undertake more careful studies of physical, physical-and-chemical, and chemical properties of the fly ash produced by any given TPP.

Thus, the objective of the project in question is the study of the use of fly ash, produced by TGC-5, as a gas-adsorbing agent in the chemical industry, and as a means to extract industrial oils and lubricants out of waste water.

The morphology of the ash particles produced by the combustion of Kuznetsk basin coal, as well as their chemical composition was studied by scanning electron microscopy (SEM) along with energy dispersive X-ray microanalysis (EDX). The obtained results are given in Figure 1 and Table 1.

The adsorption properties of the fly ash geosorbent were tested when purifying air in an ammonia synthesis shop, and upon filtering some waste water resulting from parts deoiling in machine-building. The geosorbents were dynamically tested for impurities adsorption in adsorption columns.

To remove ammonia from atmospheric air we used a mix of fly ash and hydrolyzed lignin in its polyphenebanum (PPh) form and its carbonized form (PPhc). To remove industrial oils, greases and lubricants from waste water we used fly ash and BAU-A (БАУ-А) activated carbon. As air and water media we used model systems, maximally realistic in their ammonia content and petroleum products in the form of I-12A (И-12А) industrial lubricant.

We studied the geosorbents' properties in the 4-40 °C temperature range for ammonia removal from the air, and at 22 °C when removing liquid pollutant from the waste water.

As it is evident, ash particles are porous spheres. Some pores are open, some are partially open, and some are closed. These pores are explained by bubbling of the mineral mass of silicates and aluminosilicates with some alkaline and alkaline-metal oxides and iron.

The spectra analysis demonstrated the fact that ash contains some insignificant amounts of alkaline and alkaline-metal oxides, as well as much carbon, resulting from coal dust underburning.

Thus, fly ash is porous spherical bodies consisting mainly of inorganic polymers based on aluminosilicates. The dense spherical bodies consist mainly of solidified molten silicon oxide. The underburnt carbon looks like particles of uneven and irregular shape. The oxides of alkaline-earth metals and those of other metals are found on the surface as inclusions.

The existence of pores among separate bodies, and the porosity of the bodies proper makes it possible to use fly ash as a geosorbent of gaseous and liquid pollutants.

Table 1. Content of elements in fly ash, weight. %.

	C	O	Na +K	Mg	Al	Si	Ca	Fe	other
Spectrum 1	10.73	47.09	0.77	0.68	10.74	14.35	2.01	1.26	0.43
Spectrum 2	49.68	32.20	0.74	0.33	5.82	7.01	2.37	9.23	0.44
Spectrum 3	14.48	35.57	1.15	0.91	14.91	16.51	3.66	0.15	0.81
Spectrum 4	55.88	26.94	0.67	0.29	3.42	5.71	6.26	3.26	0.83
Spectrum 5	41.18	33.48	1.78	0.23	9.06	11.79	2.01	2.80	0.47
Spectrum 6	69.37	19.30	0.52	0.37	3.15	4.39	1.79	18.8	1.12
Average	40.22	32.43	1.14	0.47	7.85	9.96	3.02	4.23	0.68

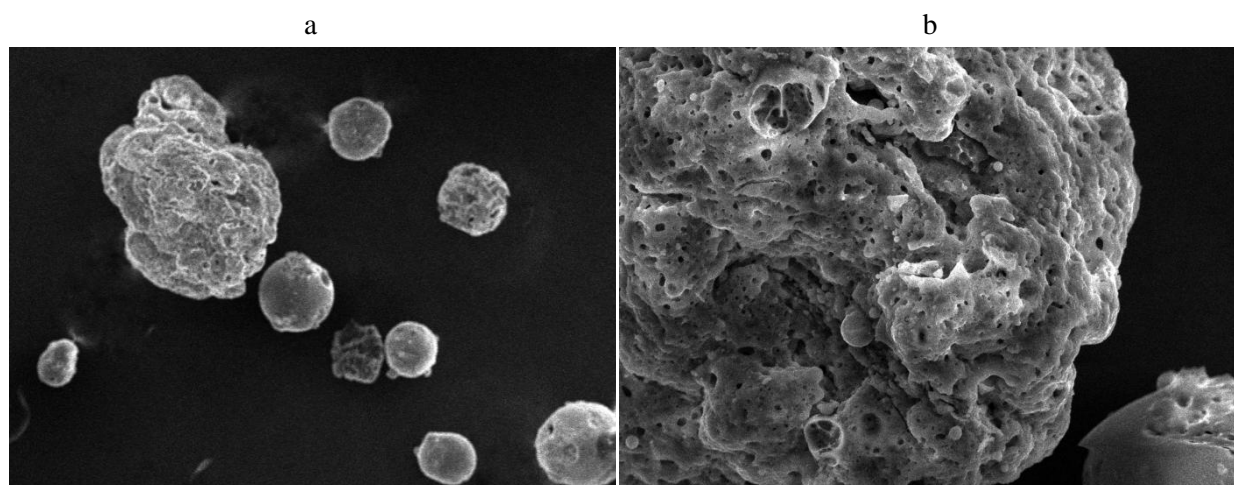


Figure 1. Fly ash morphology.

a – magnification x 100; b – magnification x 500.

To structurize the geosorbent we used some modified hydrolized lignin in its polyphhepanum (PPh) form and its carbonized residue (PPhc), resulting from burning polyphhepanum in the air at 200 °C within 15-30 minutes.

The morphology of the components in question at x500 magnification is given in Figure 2.

From the figure (Figure 2a) it is evident that the PPh particles have loose porous structure. Once the carbon is burnt out, the PPhc particles shrink, creating a structure with an increased number of micro-pores in fibers (Figure 2 b).

Table 2 gives an average aggregate element content in PPh and PPhc.

Table 2. PPh element content.

	Element content in weight. %			
	C	O	Al	Si
PPh	72.44	25.63	0.27	0.66
PPhc	64.59	34.73	0.29	0.39

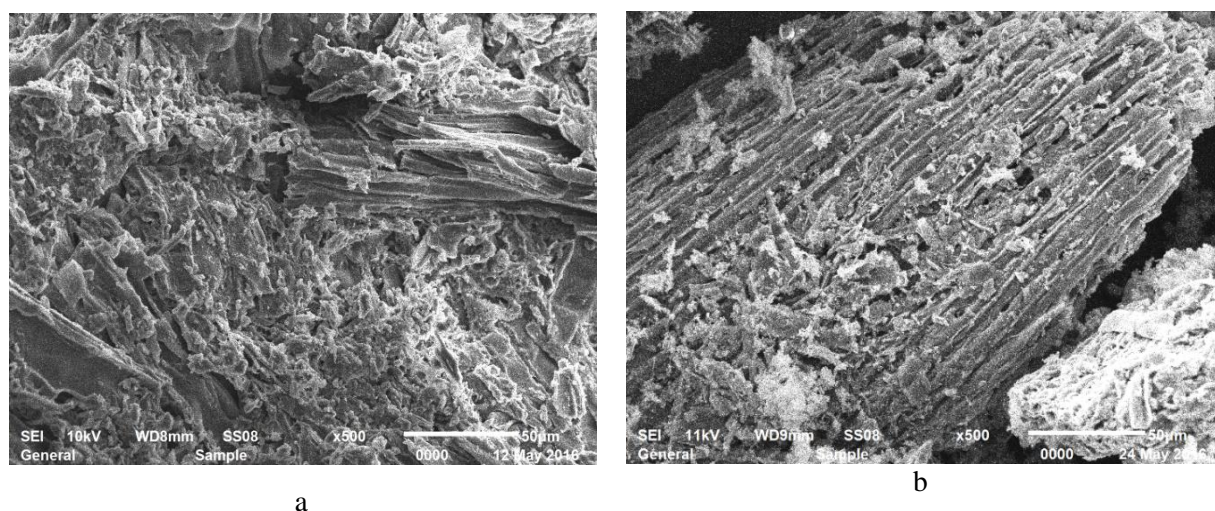


Figure 2. Morphology of PPh (a) and PPhc (b).

The EDX analysis has demonstrated that unlike fly ash both PPh and PPhc have a higher carbon content, less aluminum and silicon, while the oxygen content is virtually the same.

An efficient adsorbent's granulometric composition is very important in its creation. The granulometric composition of both the fly ash and PPh is given in Table 3.

Table 3. Granulometric composition of fly ash and PPh.

Fraction number	Particle size (μm)	Fraction percentage, %	
		Fly ash	PPh
1	> 1200	0	36.04
2	450 – 1200	2.23	48.17
3	315 – 450	2.08	7.23
4	125 – 315	52.69	7.80
5	90 – 125	36.06	0.43
6	< 90	6.94	0.33
	Total	100.00	100.00

The table clearly demonstrates that most of the fly ash particles (88.75 %) are in 315 to 90 μm size range (fractions 4-6), while the PPh particles (84.21 %) are in 450 to 1200 μm and larger size range (fractions 1-2), which can be used for adsorption purposes as well. The PPh granulometric composition after carbonization remains practically unchanged.

2. Ammonia adsorption with fly ash and PPh

The ammonia adsorption from the work area air was done with geosorbents containing fly ash and PPh in varying proportions (table 4).

The obtained results demonstrated dependency of the adsorbents' efficiency on their composition once the temperature of the contaminated atmosphere rose from 4 °C to 40 °C. With 60-80 % of fly ash content in the adsorbent the adsorption efficiency rises with the increase of temperature from 4 to 40 °C, however, when the fly ash content in the adsorbent is 20-40 %, then the adsorption efficiency goes down with the rise of temperature. The adsorption, regardless of the adsorbent composition (65-67 %), was most stable at the temperature of 20 °C.

Table 4. The adsorbent's efficiency depending on its composition in adsorbing ammonia from the air.

Temperature, oC	Fly ash percentage in the adsorbent, %			
	80	60	40	20
4	62	65	82	81
20	66	67	66	65
40	82	72	59	59

Study of the effect of PPhc on adsorption of ammonia in various concentrations. The tests were run at the temperature of 22 °C. The results of air purification through adsorption of ammonia of various concentrations are given in table 5.

Table 5. Efficiency of PPhc in adsorption of ammonia from air.

Initial concentration of ammonia-air mixture, g/m^3	Final concentration of ammonia-air mixture, g/m^3	Efficiency of adsorbent, %
4.052	0.096	97.7
6.037	0.098	98.4
8.013	0.097	98.8

The table demonstrates that the PPhc adsorption efficiency is 95-99 %, which is somewhat higher than that of the PPh and fly ash mix. Therefore, the carbonized lignin (PPhc) can be recommended as a means to increase both the efficiency and stability of a composite adsorbent based on fly ash.

3. Fly ash adsorption of petroleum products

To extract petroleum products from industrial waste water we used fly ash fractions with particle sizes of 90-125 μm and 125-315 μm . The simulated waste water contained 330-1650 mg/l of I-12A (И-12А) industrial grade oil.

The comparison results of fly ash against industrial adsorbent (BAU-A (БАУ-А) activated carbon) in clearing the waste water from industrial oil are given in Figure 3.

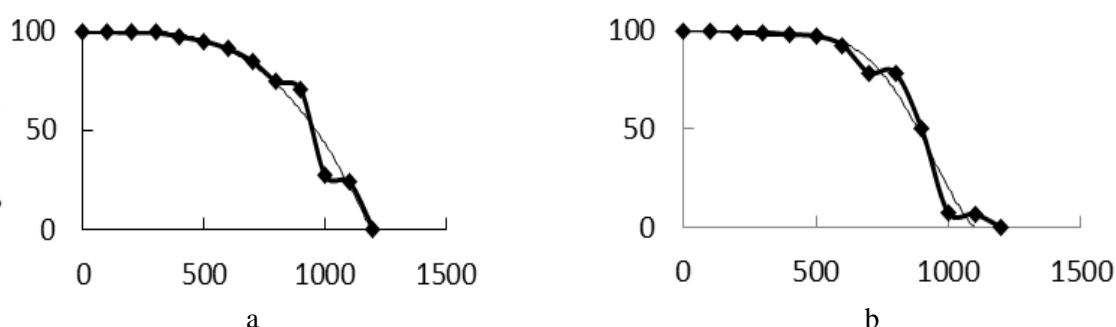


Figure 3. Waste water purification (from petroleum products) efficiency either with fly ash (a) or with activated carbon (b).

As it is evident from the Figure that when clearing the petroleum products away with fly ash (the adsorption efficiency - 98.0-98.8 %), which is a waste product of electric power production, is no less efficient as compared to activated carbon, an expensive custom product (the adsorption efficiency 98.6-99.1 %).

The mathematical analysis demonstrated complex nature of the adsorbing efficiency dependent on the put-through water volume ratio to the oil volume adsorbed either with activated carbon or fly ash. Thus, for activated carbon it is: $Y = 102.5 - 0.0697x + 0.0003x^2 + 0.7x^3$, while for the fly ash adsorption it is $Y = 99.041 + 0.0071x - 0.6x^2 + 0.8x^3$, where Y – adsorption efficiency, X – waste water volume.

Therefore, when planning some larger-scale purification facility, it is still possible to get high-grade purification of large volumes of petroleum-bearing waste water, thus, solving the problem of waste utilization upon recycling these waters.

With ammonia as an example, it has been demonstrated that a highly-efficient composite geosorbent can be obtained from fly ash, left after burning Kuznetsk basin coal at high temperature, and the carbonized polyphosphanum, obtained at burning lignin at low temperature as to conserve its porous structure. So, this mix is a highly-efficient gas geosorbent.

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