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A.U. Khabashova[1] – *main author*,
A.N. Nurlybayeva[2], **U.G. Kanatbek**[3],
A.A. Kuanyshbek[4], **A. Kurtebayeva**[5],
S. Orynbayev[6], **T.G. Helder**[7], **M.S. Kalmakhanova**[8]

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[1,5]PhD student, [2]PhD, Associate Professor, [3]Laboratory assistant, [4]Master student, [6,8]PhD, Associate Professor, [7]Professor

ORCID
[1]https://orcid.org/0009-0008-8956-9960 [2]https://orcid.org/0000-0001-9904-9979
[3]https://orcid.org/0009-0005-4568-9993 [5]https://orcid.org/0000-0002-1975-0755
[6]https://orcid.org/0000-0002-5077-7219 [7]https://orcid.org/0000-0001-6898-2408
[8]https://orcid.org/0000-0002-8635-463X

[1,2,3,4,5,6,8]M.Kh. Dulaty Taraz University, Taraz, Kazakhstan
[7]The Polytechnic Institute of Bragança, Bragança, Portugal

@ *[1]zhigerbaevaa@mail.ru*

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DEVELOPMENT OF NEW MATERIALS BASED ON AGRO-INDUSTRIAL WASTE FOR THE STORAGE OF A PERMEABLE REACTIVE BARRIER

Abstract. Rapid industrialization, expanding urbanization, and unrestrained use of natural resources contribute to environmental issues, particularly the contamination of water bodies by a variety of chemical compounds due to inadequate wastewater treatment. These contaminants, referred to as contaminants of emerging concern (CECs), pose global challenges due to their widespread occurrence, persistence, and bioaccumulation, stemming from anthropogenic activities. Notable examples of CECs include pharmaceuticals like paracetamol and synthetic chemicals such as perfluorooctanoic acid (PFOA), underscoring the imperative for effective wastewater treatment. Furthermore, phenolic species originating from pharmaceutical and dye industries endure in wastewater, posing threats to human health and ecosystems. To address these challenges, permeable reactive barriers (PRBs) have been developed to treat polluted waters, utilizing various materials. However, concerns about their manufacturing complexity processes have prompted the exploration of simpler and eco-friendly alternatives. Promising options include geopolymers, activated carbons derived from waste, and carbon nanotubes sourced from plastic solid waste. Integrating these materials into permeable barriers and adopting the concept of PRBs, with a focus on circular economy principles, presents a sustainable approach to mitigate population exposure to contaminated water. This innovative strategy not only addresses the environmental and health risks associated with water pollution but also aligns with the broader purpose of this work, which is to produce environmentally friendly permeable barriers for application in systems post wastewater treatment plants.

Keywords: contaminants of emerging concern, heavy metal, permeable barriers, wastewater treatment.

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Introduction. That being stated, certain contaminants of emerging concern (CECs) in different aquatic environments mainly come from anthropogenic activities. Their extensive occurrence, persistence, bioaccumulation, constant circulation, migration, and transformation in environmental media have generated a substantial global concern [1]. Among pharmaceutical compounds that are CECs and cause water pollution, paracetamol (acetaminophen, 4-acetylaminophenol) deserves particular attention since it has recently been discovered as a potential pollutant of waters [2]. Another example of a CECs belonging to a group of synthetic chemicals called per- and polyfluoroalkyl substances is perfluorooctanoic acid (PFOA), which even became part of the Stockholm Convention on Persistent Organic Pollutants in 2019.

In addition to the mentioned contaminants, phenolic compounds in wastewater caused by the pharmaceutical or dye industries are persistent organic pollutants resistant to decomposition/degradation and cause harmful severe effects on human health and the environmental ecosystem [3]. The phenolic pollutants and their metabolites in living cells cause mutagenicity and carcinogenicity. Furthermore, some phenolic compounds, such as chlorophenols, nonylphenols, and 4-tert-octylphenol, can block normal hormonal functions, mimic natural hormones, occupy their receptors in different organisms, and cause severe hormone imbalance and health hazards.

Creating a new approach to environmental protection across different domains involves utilizing strategies for minimizing contaminants in wastewater treatment plants (WWTP), informed and enhanced by advancements in groundwater remediation techniques. Previous efforts to remediate polluted groundwater have culminated in the development of permeablereactive barriers (PRBs). They are subsurface filters filled with appropriate materials to treat through-flowing polluted waters. Although many naturally occurring and inexpensive materials are manufactured in methods that can harm the environment. So, there is still a need to look for an absorbent to use appropriately in permeable barriers, with high efficiency, economy, effectiveness, and manufacturing with greenways without any adverse side effects on the environment [4].

There are numerous papers on PRBs, most of which focus on removing contaminants with multi-barrier systems so that high concentrations of contaminants are significantly reduced to a minimum [5-10]. Thus, by implementing the concept of PRBs in permeable barriers (PB) in the WWTP and employing economically efficient reactive materials sourced from waste, a connection can be established with the principles of circular economy and sustainable development. This approach aims to reduce the population’s exposure to contaminated water and contributes to resource efficiency and environmental sustainability.

Materials and methods. *Reactants and materials used.* Buffer solutions for calibrating the pH meter, kits for determining ions (nitrates, phosphates, sulfates) and heavy metals (lead, cadmium, etc.), indicator strips for quickly determining the concentration of certain parameters (pH, water hardness). Sawdust – for the production of activated carbon, activated carbon,distilled water, KOH – for the oxidation of activated carbon, model solutions with heavy metals: $Cr_2(SO_4)_3\ 6H_2O$, to regulate the pH value in model solutions with heavy metals, added acid and base: C(NaOH) = 0.01 mol/dm^3, C(HCl) = 0.01 mol/dm^3.

FTIR analysis was used to determine the physico-chemical characteristics of pumpkin seed shells. IR spectra of pumpkin seed shells were obtained on an IR

Fourier device (Infraspec, model FSM 2202, Russia, St. Petersburg) with a resolution of 1 cm^{-1} and a scanning range of 5000-500 cm^{-1} using a sample. Scanning electron microscope JSM-6490LV with INCA Energy Energy microanalysis and HKL-Basic structural analysis systems. The multi-purpose scanning electron microscope (useful magnification of 300,000) combines the possibilities of working in both standard and low-vacuum modes. Allows you to examine samples without spraying with a conductive layer. Additionally, it is equipped with an INCA Energy 350 energy dispersive microanalysis system and a prefix for studying the texture and structure of polycrystalline HKL Basic samples. The concentration of Cr (III) was determined by the NPP method. All measurements were carried out using Agilent 4200 MP-AES equipped with an Agilent 4107 nitrogen generator. The sample entry system consisted of a double-pass cyclone spray chamber, an OneNeb sprayer, a Solvaflex pump tube (orange/green) and an Easy-fit burner for sample introduction. Multi-element calibration standards containing Cr (III) with a concentration of 50 mg/l were used. The standard was prepared in an environment of 5% HNO_3/0.2% HF (vol./vol.) (US production). The pH was determined using a pH meter of the brand pH-009(1)A.

Development of materials. First of all, the sawdust was left in distilled water for 12 hours.After 12 hours, the sawdust was filtered out. It was left at room temperature until the water evaporated. After evaporation of the water, it was dried for 3 hours at a temperature of 70°C in a vacuum oven. At this stage, the material was burned in a furnace at 320°C for 1 hour. The nitrogen furnace program was adjusted to 320°C, and then the suspended sawdust was burned for 1 hour. The resulting coal was compared before and after it was placed in the furnace, the mass of coal lost during gorenje was calculated and subtracted from the initial mass. And I received about 3 g of the material. After obtaining coal at 320°C, it was activated in two ratios - 1:1, 2:1. To obtain activated carbon with a concentration of 1:1, 1 g of KOH and 1 g of carbon burned at 320°C were consumed.

Influence of contact time. 0.2 g of 100 ml of this 2:1 activated carbon concentration was left to be stirred on a magnetic stirrer for 24 hours in time. We took 0.4 g of a 50 mg/l $Cr(SO_4)_3 \cdot 6H_2O$ model solution, put it in a 1 liter flask and mix it to the line with water. The prepared solution was diluted to 25 ml, determined by the method of APP spectroscopy, a calibration table was built, checked and established that the model solution was purified at the same time. At different intervals, 100 ml of the model solution was poured into a 250 ml flask at 0 minutes and mixed. During this time, 2 ml were taken for 0 minutes and poured into a 25 ml flask. After 0 minutes of sampling, 0.2 g of activated carbon was added to a flask filled with 250 ml of the model solution in a ratio of 2:1. Every minute indicated in the table, 2 ml of the solution was taken and drained into a flask with a capacity of 25 ml. That is, small filters were installed in a flask with a capacity of 25 ml, filter paper was installed on the surface, 2 ml was poured, and topped up.

Research results and discussion. *Results of agrochemical soil analysis.*Soil samples were taken from two different places. The first sample was collected at a depth of 0-15 cm near the septic tank in the village of Asa, Zhambyl district, and the second sample – at a depth of 0-10 cm from the place of sowing for animal feed. All samples were taken with special equipment – a soil sampler (MemST 26205-91). Determination of mobile compounds of phosphorus and potassium by the Matsevina method in the modification of Tsinao (MemST 26423-85). Methods for determining the specific conductivity, pH and water absorption of solid residue

(MemST 26423-85-26428-85). Methods for determining calcium and magnesium in an aqueous extract. (Fig. 1).

Samples were taken at a depth of 0-15; 15-30 in the first place and 0-10; 10-20; 20-30 in the second place. All samples were taken with special soil sampler equipment. We had the most popular type of soil sampler – a manual soil drill, model “AM-16”, which is designed to take soil samples with a violation of their structure, as well as to measure the depth of soil freezing, as well as for drilling wells for permafrost meters.

Fig. 1. Soil sampling process

The results showed that the average soil pH in Asa village was 7.5, which is slightly above the optimal range for crops. This may be due to anthropogenic pressure, which may interfere with the conversion of organic matter into plant-available mineral compounds.

The analysis of the amount of humus in the soil was carried out only on the second plot. The results showed a very low humus content in the upper soil layers, which indicates unfavourable conditions for the development of plant roots at certain depths. This is typical for some types of soil, such as podzolic or clay-podzolic.

pH = 6.26 is the soil acidity level that affects the availability of nutrients to plants. The optimum pH for most crops is considered to be 6-7 (Table 1).

Table 1

Main agrochemical characteristics

№	Place of selection and depth	Determined indicators				
		General Humus, %	Movable			pH
			Nitrogen mg/kg	Phosphorus mg/kg	Potassium mg/kg	
1	P-1; 0-15		162.4	134	290	6.26
2	P-2; 15-30		142.8	106	210	5.86
3	P-1; 0-10	0.70	33.6	10	190	8.33
4	P-2; 10-20	0.83	33.6	8	180	8.46
5	P-3; 20-30	0.59	36.4	6	170	8.57

The results of the agrochemical analysis of the soil for the sampling site P-1 at a depth of 0-10 cm are shown in Table 1. Analysis of these data allows us to assess the fertility of the soil and its suitability for growing crops. High pH levels can affect the availability of certain nutrients to plants, such as phosphorus. Low humus content may indicate the need to improve the soil with organic fertilizers or green manure.

The data show the concentration of various elements and ions in the aqueous extract of the soil (Table 2). Based on the results of the analysis of the aqueous extract of the soil, the following conclusions can be made:

Salts: The total soil salinity is 0.122%, which is an important indicator for assessing soil fertility and its suitability for agriculture.

Alkalinity: The amount of bicarbonate ion (HCO_3^-) varies from 0.027% to 0.44%, indicating the alkalinity of the soil. This parameter is important for optimal plant growth.

Table 2

Water extract

№	Water extract in $\frac{\%\%}{м.экв}$ on absolutely dry soil								
	Total salts, %	Alkalinity		Cl^-	SO_4^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
		Total in HCO_3^-	From normal carbonates to CO_3						
1	0.122	0.027		0.001	0.066	0.008	0.015	0.005	0.001
		0.44		0.04	1.37	0.38	1.24	0.21	0.02
2	0.177	0.027		0.000	0.109	0.011	0.022	0.007	0.001
		0.44		0.00	2.27	0.57	1.81	0.30	0.02
3	0.179	0.029		0.000	0.110	0.008	0.026	0.006	0.001
		0.48		0.00	2.28	0.38	2.10	0.27	0.02

Chlorides, sulfates, calcium, magnesium, sodium, potassium: The content of these elements is also varied and varies widely. These elements play an important role in plant nutrition and metabolism. Soil pH 8.33 indicates an alkaline environment. This parameter is important for the availability of nutrients to plants. Total humus: the humus content is 0.70%, which is important for improving the structure and fertility of the soil.

Based on this data, it is possible to draw conclusions about the chemical composition of the soil and its suitability for farming. Further research and analysis will help determine the optimal measures to increase soil fertility and ensure optimal conditions for plant growth and development.

As we already know, the value of the cation exchange capacity depends on the granulometric composition of the soil, or more precisely on the silt content (Table 3).

Table 3

Content of soil granulometric composition

№	Place of selection	Depth	A.S.N. % H_2O	Fraction content in % on absolute dry soil						
				Fraction sizes in mm						
				Sand		Dust			Silt	3-x
				1.0 -0.25	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001	Factions < 0.01
1	P-1	0-15	1.72	19.434	45.157	18.722	4.477	11.396	0.814	16.687
2	P-2	15-30	1.44	20.901	36.080	27.192	2.029	7.305	6.494	15.828
3	P-3	0-10	0.98	7.049	47.304	16.966	2.020	17.370	9.291	28.681
4	P-4	10-20	0.82	6.917	50.333	13.712	8.469	18.552	2.017	29.038
5	P-5	20-30	0.94	5.492	36.362	17.363	13.325	23.420	4.038	40.783

According to our data, the silt content varies from 0.8-4.038%, and the physical sand is 19.434-5.492, which means that the sand content decreases with depth. Classification of soils by granulometric composition for stony soils should be accompanied by indications of the degree of their stonyness. According to our data, the first sampling location is dominated by a greater sand content, as in other soil layers.

Based on the results of the study, the indicators of total soil contamination were calculated taking into account toxicity in all variants of the studied variants and in the filtration area. Assessing the obtained contamination indicators according to the scheme for assessing agricultural soils, these soils can be characterized as having an acceptable degree of contamination (less than 16.0) (Table 4).

Table 4

Microelement content

№	Place of selection	Depth	Mobile forms of microelements, mg/kg			
			Zn	Cu	Cd	Pb
1	P-1	0-15	131.8	16:30	1.10	1.60
2	P-2	15-30	71.6	8.40	0.50	1.40
3	P-3	0-10	3.10	0.80	0.70	1.70
4	P-4	10-20	3.80	1.30	0.60	1.50
5	P-5	20-30	2.80	1.20	0.90	1.60

At the sampling site near the canal is 6,048.07 and is classified as acceptable. The maximum environmental indicator of total pollution at the first sampling site is 131.8 due to the concentration of cadmium compounds and zinc compounds, which are elements of hazard class 1. At the filtration site, the indicator is 3.10. In all the studied options, during the growing season, there is a fluctuation in the content of mobile copper compounds and a decrease in depth, no excess of MPC is noted. The highest copper content in the soil is observed at the first site near the canal - 16.30 mg/kg, on the filtration field 0.70 mg/kg. Zn mobility is associated with acidification of hydrolytic acidity due to the use of mineral fertilizers. Cadmium is not among the elements necessary for plants, moreover, it is considered to be especially dangerous for plants and the vital activity of animals and humans. Therefore, constant monitoring of the cadmium content in the soil and plants is required. The level of soil pollution with heavy metals is established based on the content of mobile compounds and their compliance with maximum permissible concentrations. It was established that the content of mobile cadmium compounds in the soil was 1.0-0.9 mg/kg, and is decreasing with depth, which exceeds the MAC value.

Thus, the content of total cadmium and zinc compounds exceeds the Clarke values, but the calculated environmental indicator of total pollution, taking into account toxicity, is acceptable for the use of land in agriculture. The studied variants revealed a low content of mobile copper and zinc. Contents

mobile form of cadmium exceeding the maximum permissible concentration of soil on fallow land under no-till technology. The obtained results indicate the need for constant close attention to the problem of optimizing the microelement balance of arable soils, the importance of which increases in soil health management.

Scanning Electron Microscopy. Figure 2 shows the SEM images of activated carbon obtained from sawdust at a concentration of 2:1 at 720°C. This Figure 3.1 shows the surface of activated carbon particles obtained from sawdust at a concentration of 2:1. During the carbonization process, the structure of the shell changes. As shown in this image, as a result of heat treatment, holes and irregularities are visible on the surface of the activated carbon particles, which were previously closed and not connected to the pore space. The increase in temperature can be explained by the fact that wood chips cause thermal decomposition of organic matter, so the number of pores and irregularities increases. The internal structure and thick cell walls are shown.

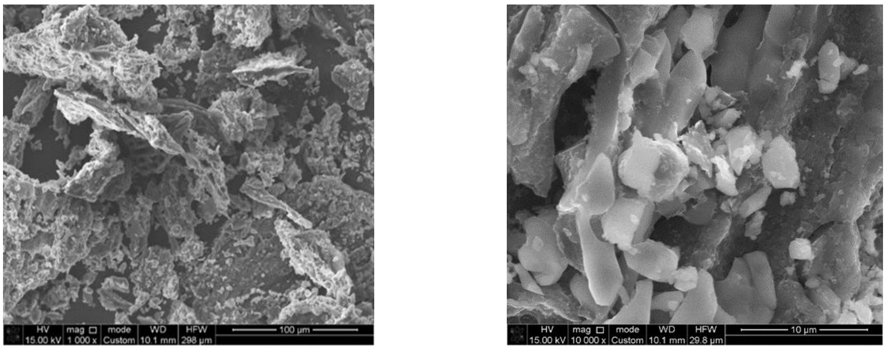

Fig. 2. SEM images of activated carbon obtained from sawdust at a concentration of 2:1, obtained at 720°C

Adsorption of heavy metal with the activated carbon. To determine the effect of the adsorbent mass on the adsorption process, 10 different weighed portions of each sample (m(adsorbent) = 0.2; 0.4; 0.6; 0.8; 0.10 g; 0.12 g; 0.14 g; 0.16 g; 0.18 g; 0.20 g) were prepared and studied. An adsorbent with a concentration of 2:1 was chosen as a sample, that is, taken from sawdust burned at 720°C (0 min, 15 min, 30 min, 60 min, 1.5 h, 2 h, 4 h, 6 h, 8 h, 24 h). According to the results of the studies, the adsorption of heavy metal ions Cr^{3+} increased due to the increase in mass. The yield of the adsorbent for the heavy metal ion Cr^{3+} 0.2 g/l – 49.375; 0.4 g/l – 15.25; 0.6 g/l – 16,625; 0.8 g/l – 13,125; 0.10 – 12,125; 0.12 – 7.5; 0.14 – 5,625; 0.16 – 5,625; 0.18 – 2.5; It achieved low values of 0.20-0.125. These results were due to the increase in surface area of 2:1, and Cr^{3+} performed moderately well compared to other adsorbents. The obtained results are shown in Figure 3.

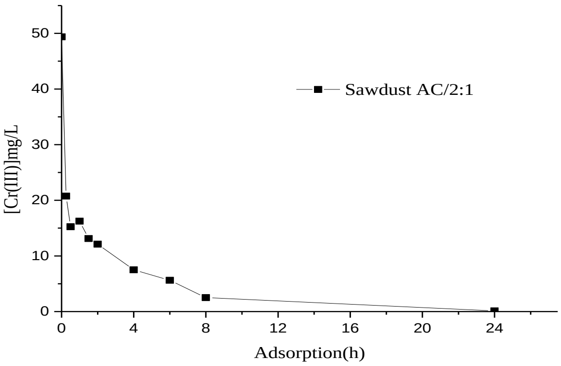

Fig. 3. Adsorption of heavy metal with the activated carbon at a concentration ratio of 2:1

The graph shows the results of the adsorbent analysis by atomic emission spectroscopy. According to the results obtained, it was noted that over time it was well purified.

Conclusion. In modern conditions, biomass waste is an accessible, renewable and cost-effective resource that can be used to produce popular and environmentally friendly materials. The study assessed results of the experiment demonstrated that activated carbon from wood biomass is an effective means for removing heavy metals from aquatic environments. The two tested adsorbents showed a high degree of purification, which proves their promise for further use in water purification from heavy metals. Thus, the developed adsorbent has great potential for large-scale use in environmental technologies.

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**А.У. Хабашова[1], А.Н. Нурлыбаева[1], У.Г. Канатбек[1], А.А. Куанышбек[1],
А. Куртебаева[1], С. Орынбаев[1], Т.Г. Хельдер[2], М.С. Калмаханова[1]**

[1]М.Х. Дулати атындағы Тараз университеті, Тараз қ., Қазақстан
[2]Браганса политехникалық институты, Браганса қ., Португалия

ӨТКІЗГЕН РЕАКТИВТІ КЕЛДІ САҚТАУ ҮШІН АУЫЛ ШАРУАШЫЛЫҒЫ ҚАЛДЫҚТАРЫНЫҢ НЕГІЗІНДЕ ЖАҢА МАТЕРИАЛДАРДЫ ӘЗІРЛЕУ

Аңдатпа. Қарқынды индустрияландыру, өсіп келе жатқан урбанизация және ресурстарды бақылаусыз пайдалану экологиялық проблемалардың пайда болуына, атап айтқанда, ағынды суларды тиісті түрде тазартпау салдарынан су объектілерінің әртүрлі химиялық қосылыстармен ластануына ықпал етеді. Бұл ластаушы заттар, алаңдаушылық туғызатын заттардың ластаушы заттары (ЦЭҚ) антропогендік әрекеттер нәтижесінде пайда болатын кең таралған, тұрақтылығы және биоаккумуляциясы бойынша жаһандық проблемалар болып саналады. Парацетамол сияқты фармацевтикалық препараттар және ағынды суларды тиімді тазартуды қажет ететін перфтороктан қышқылы (PFOA) сияқты синтетикалық химиялық заттар CEC-тің белгілі мысалдары болып табылады. Сонымен қатар, фармацевтика және бояу өнеркәсібінде өндірілетін фенолдық түрлер адам денсаулығы мен экожүйеге әсер етпес бұрын ағынды суларға әкеледі. Осы мәселелерді шешу үшін әртүрлі материалдарды пайдалана отырып, ластанған суларды тазарту үшін өткізгіш реактивті кедергілер (PRBs) әзірленді. Дегенмен, олардың өндірістік процестерінің күрделілігі туралы алаңдаушылық қарапайым және экологиялық таза баламаларды зерттеуге түрткі болды. Перспективті нұсқаларға геополимерлер, қалдықтардан алынған белсендірілген көмір және пластикалық қатты қалдықтардан алынған көміртекті нанотүтіктер жатады. Бұл материалдарды өткізгіш кедергілерге біріктіру және оларды жүзеге асыру. PRB концепциясы айналмалы экономика принциптеріне назар аудара отырып, ластанған судың планетаға әсерін азайтудың тұрақты тәсілі болып табылады. Бұл инновациялық стратегия тек тәуекел мәселелерін қарастырмайды. судың ластануымен байланысты экологиялық және денсаулық мәселелері, сонымен қатар бұл жұмыстың неғұрлым тиімді мақсаттарына жауап береді, яғни сарқынды суларды тазартудан кейін үйде пайдалану үшін экологиялық таза өткізгіш кедергілерді жасау.

Тірек сөздер: жаңадан пайда болатын ластаушы заттар, ауыр металл, өткізгіш баргерлер, ағынды суларды тазарту.

**А.У. Хабашова[1], А.Н. Нурлыбаева[1], У.Г. Канатбек[1], А.А. Куанышбек[1],
А. Куртебаева[1], С. Орынбаев[1], Т.Г. Хельдер[2], М.С. Калмаханова[1]**

[1]Таразский университет им. М.Х. Дулати, г. Тараз, Казахстан
[2]Политехнический институт Браганса, г. Браганса, Португалия

РАЗРАБОТКА НОВЫХ МАТЕРИАЛОВ НА ОСНОВЕ АГРОПРОМЫШЛЕННЫХ ОТХОДОВ ДЛЯ ХРАНЕНИЯ ПРОНИЦАЕМОГО РЕАКТИВНОГО БАРЬЕРА

Аннотация. Быстрая индустриализация, расширяющаяся урбанизация и неконтролируемое использование природных ресурсов способствуют возникновению экологических проблем, в частности, загрязнению водоемов различными химическими соединениями из-за неадекватной очистки сточных вод. Эти загрязняющие вещества, называемые загрязняющими веществами, вызывающими обеспокоенность (CEC), представляют собой глобальные проблемы из-за их широкого распространения, стойкости и биоаккумуляции, возникающих в результате антропогенной деятельности. Известными примерами CEC являются фармацевтические препараты, такие как парацетамол, и синтетические химикаты, такие как перфтороктановая кислота (PFOA), что подчеркивает необходимость эффективной очистки сточных вод. Кроме того, фенольные виды, происходящие из фармацевтической и красильной промышленности, сохраняются в сточных водах, представляя угрозу для здоровья человека и экосистем. Для решения этих проблем были разработаны проницаемые реактивные барьеры (PRB) для очистки загрязненных вод с использованием различных материалов. Однако опасения по поводу сложности процессов их производства побудили к исследованию более простых и экологически чистых альтернатив. К перспективным вариантам относятся геополимеры, активированный уголь, полученный из отходов, и углеродные нанотрубки, полученные из твердых пластиковых отходов. Интеграция этих материалов в проницаемые барьеры и принятие концепции PRB с упором на принципы круговой экономики представляет собой устойчивый подход к смягчению воздействия загрязненной воды на население. Эта инновационная стратегия не только решает проблемы рисков для окружающей среды и здоровья, связанных с загрязнением воды, но и соответствует более широкой цели этой работы, которая заключается в создании экологически чистых проницаемых барьеров для применения в системах после очистных сооружений сточных вод.

Ключевые слова: загрязнители вызывающие новую озабоченность, тяжелый металл, проницаемые барьеры, очистка сточных вод.