The Effectiveness of Some Coal-Based Mineral Compositions in the Decontamination and Environmental Protection of the Small Urban Rivers' Watery

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Abstract

The effectiveness of the "T"-brand coal processing sludge, technical pyrocarbon, and their mixture as adsorbents for the decontamination of drainage water from organic pollutants has been investigated. The contaminated water samples were collected from the ordinary car filling/service station's drainage system and then treated with the adsorbents. Water absorbance and chemical oxygen demand (COD) were controlled as the water quality and decontamination effectiveness parameters.

A 4:1 mixture of coal refinery sludge and technical pyrocarbon was used as the most efficient adsorbent for mixed petrochemical and mechanical pollution agents. It has been found that this composition effectively decontaminates water from mixed organic pollutants. The water cleaning cartridges filled with this composition of adsorbents showed high decontamination performance eliminating about 85 % of petrochemical water pollution agents. This performance does not degrade much, and a 4 kg adsorbent load should be sufficient to treat an amount of wastewater formed at the car filling station for at least one month.

Keywords: *small urban rivers, oil-contaminated water, adsorption water treatment, mixed coal adsorbents, pyrocarbon*

Introduction

A significant part of the total water contamination comes from various low-capacity sources such as isolated local drainage systems, car filling, washing and service stations, industrial and agricultural storage facilities, and other objects not connected to the centralized sewage system. The impact of each such facility may not be serious as it does not produce a significant amount of pollution, but when several of them discharge their waste/drainage water into the same small river or stream, the cumulative effect can be devastating [1–3]. Oil-containing wastewaters are especially dangerous, and the irregular character of their discharge additionally increases their environmental threat.

Small enterprises like car filling stations usually are not equipped with the specific water treatment units to catch or clean the oil components and, as a result, their wastewater and/or drainage water are discharged to the local household sewage system or even to the nearby water bodies without any specific treatment. Many small urban rivers and ponds turned into dead water bodies because of this practice [4, 5].

It should be noted that mixing and dilution of the drainage/wastewater can bring the content of toxic compounds close to or within the sanitary standards; however, this approach does not decrease the total amount discharged to the river or stream nor does it ease the anthropogenic load. Small rivers bring pollutions to the larger rivers they merge with and, as the transport network develops, this problem becomes more and more acute.

Typical car service/filling/washing station discharges 0.7–1.2 m^3 of untreated wastewater per day with the content of suspended particles 800–3000 mg/L (up to 0.3%) and 500–900 mg/L (up to 0.09%) of oil products. The maximal permissible concentration (MPC) of these agents in the treated wastewater before discharging should be under 0.75 and 0.3 mg/L, respectively [6]. Full-scale water treatment equipment cannot be effective for cleaning such a small amount of wastewater, while smaller mobile water treatment modules can be considered as a better solution. Given the nature of typical water pollution agents, the mosaic surface coal-like materials should be effective adsorbents for such modules. High adsorption effectiveness of various coal-like materials was reported for some individual organic pollutants [7, 8] and mixed petrochemical pollutions [6, 9, 10]. As found previously [6], a 4:1 mixture of coal refinery sludge and technical pyrocarbon is quite effective in various applications designed to extract organic water contamination agents. Both components are readily available as by-products from the coal refinery and organic waste incineration facilities [11]. It should also be noted that petrochemical pollution agents are traditionally considered to be poorly soluble in water components, which are found in the surface layer. However, rather a significant solubility may be reached due to other chemicals present in the mixture. As a result, part of the petrochemical pollutants can be transferred into the bulk of the liquid phase. This process can be realized by the "bridging" of organic compounds adsorbed on the adsorbent's surface from a non-aqueous phase and then desorbed to the aqueous phase [12]. Besides, the solubility of petrochemicals can be increased because of some detergents and surfactants co-present in the mixture, which

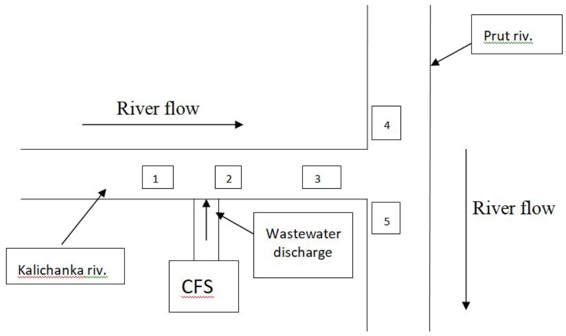

Fig. 1. Sampling area scheme: Point 1 – 50 m upriver from the car filling station (CFS) wastewater/drainage water discharge point; 2 – 20 m downriver from the discharge point; 3 – 2000 m downriver from the point of discharge; 4 – water of the river of Prut upriver from the point of confluence; 5 – 30 m downriver from the confluence

Rys. 1. Schemat obszaru pobierania próbek: Punkt 1 – 50 m w górę rzeki od punktu zrzutu ścieków/ wód drenażowych na stacji paliw; 2 – 20 m w dół rzeki od punktu zrzutu; 3 – 2000 m w dół rzeki od punktu zrzutu; 4 – wody rzeki Prut w górę rzeki od punktu zbiegu; 5 – 30 m w dół rzeki od zbiegu

cause the emulsification or solubilization of petrochemicals and result in the formation of an aqueous colloidal solution. All these reasons should be taken into consideration while selecting the most effective adsorbent, which must combine the hydrophobic and hydrophilic surface spots.

Based on the above, a 4:1 mixture of coal sludge and technical pyrocarbon was used in this work to investigate its effectiveness and the ways of its possible application to the decontamination of low-scale wastewater discharges from small car filling/washing/service facilities. The adsorption effectiveness of both individual components was also checked to compare it with the effectiveness of the 4:1 mixture.

Materials and experimental methods

The investigation was done with the surface water samples taken from a small river of Kalichanka near its confluence with a larger river of Prut and from the Prut within the city limits of Chernivtsi, Ukraine. A scheme of the sampling points is shown in Fig. 1. All samples were taken in the dry weather from the surface water in such a way as to avoid their additional pollution with the river mud and other similar materials.

The sludge with an ash content of 43.1% and a moisture content of 15.3% obtained after refining the "T" brand coal was used as a mosaic surface (hydrophilic/hydrophobic areas) component, and technical pyrocarbon with an ash content of 28% and a moisture content of 1.6% obtained after pyrolysis of mixed organic polymer waste was used as a hydrophobic component of the adsorption composition. The component's (sludge/pyrocarbon) mass content in the mixture was 4:1.

The components were ground individually or as a mixture in a ball mill with a standard set of steel grinding ball elements. Then a mixture of the particles ranging in size from 0.5 to 50 μm was sieved out and used in further experiments.

Since the petrochemical pollutants and suspended particles are expected to be the most influential water contamination agents, we measured the COD and absorbance of the samples to evaluate the effectiveness of water decontamination.

The absorbance (1) and COD (2) of the samples were measured by the following procedures.

(1) A water sample was poured into a 10 mm cuvette, and then its absorbance was measured by the KFK-3 photocolorimeter by LOMO at the wavelength 540 nm against distilled water. If some adsorbent had to be added, it was poured into the water then the mixture was kept for 30 min at periodical stirring to reach the adsorption equilibrium. Finally, the adsorbent was filtered out, and the absorbance of the filtrate was measured as described above.

(2) – expressed method. A water sample was filtered through the paper filter, and then 5 mL of the filtrate was poured into a 250 mL thermal-proof flask. Then we added 5 mL of a 0.1 N aqueous solution of potassium dichromate, stirred the mixture, and, drop by drop, added 15 mL of concentrated sulfuric acid at constant stirring. The solution was kept for 5 min with constant stirring, then cooled to 20°C. Finally, it was diluted with 50 mL of distilled water and titrated by a 0.1 N solution of Mohr's salt against the ferroin indicator. The same procedures were performed with a control sample containing distilled water instead of the filtrate.

The following formula was used to calculate COD:

$$COD = 1.2 * ((V_0 - V) * 0.1 * 8 * 1000 / a) - 18.5,$$

where V_0 and V – amounts (mL) of a Mohr's salt solution used for the titration of the samples of control and working solutions, 0.1 – normality of a Mohr's salt solution, 8 – the chemical equivalent of oxygen, α – water sample amount (mL), 1.2 and 18.5 – correcting coefficient to agree the results of this expressed and the standard arbitration experimental measurements of COD.

Table 1 represents the average COD values for all sampling points.

No significant changes in the pollution agents' concentrations were found in samples taken in dry weather during spring-autumn seasons. The COD of the samples varied within ± 15% at every particular sampling point. On the other hand, it was found that petrochemicals and suspended particles are rather persistent agents affecting the entire area of investigation. COD does not decrease much even in 2000 m downstream from the point of discharge (compare the COD of samples 2 and 3, Table 1). The influx of the Kalichanka into the Prut has a serious negative impact, causing an increase in COD from 7.2 to 12.5 mg O/L. It should be noted that the maximal permissible value of COD in an open freshwater body must be below 5 mg O/L. So, it was exceeded even upriver from the confluence, but downstream it became more than twice higher.

Tab. 1. COD of the water samples (average statistical deviation less than ± 15 %)
Tab. 1. ChZT próbek wody (średnie odchylenie statystyczne poniżej ± 15%)

COD value, mg O/L	Sampling point				
	1	2	3	4	5
	11.2	18.3	16.8	7.2	12.5

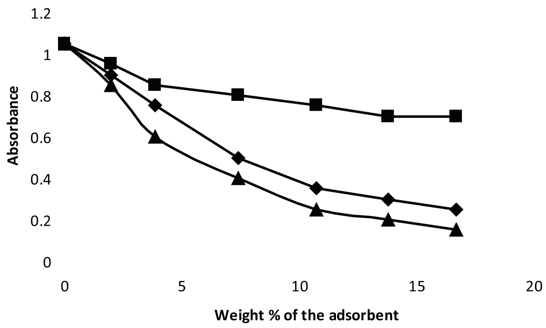

Fig. 2. The dependence of the samples' absorbance on the added amount of various adsorbents. ◆ – coal refining sludge; ■ – technical pyrocarbon; ▲ – 4:1 mixture of the sludge and pyrocarbon

Rys. 2. Zależność absorbancji próbek od dodanej ilości różnych adsorbentów. ◆ – muł z rafinacji węgla; ■ – pirocarbon techniczny; ▲ – mieszanina 4:1 mułu i pirocarbonu

The following experiment was taken to evaluate the effectiveness of water cleaning with a mixture of adsorbents. Ten liters of contaminated water were placed in a plastic canister connected to the cartridge filled with 1 kg of the mixture. Then the water was passed through the cartridge with a flow rate of 1 L/min. Control samples of the treated water were taken after the cartridge and then analyzed to determine their absorbance and COD, as described above.

Results and Discussion

As seen from the data above, the river of Kalichanka is significantly contaminated with organic pollutants providing additional anthropogenic load on the river of Prut. Waste/drainage water discharge from the local CFS negatively contributes to total river water contamination. Therefore, some approaches to wastewater decontamination should be considered.

Since the absorbance of a sample depends on the content of suspended particles, this parameter can be used to characterize the effectiveness of extraction of suspended pollutants from water. Fig. 2 represents the dependence of the samples' absorbance on the added amount of various adsorbents.

The COD of a water sample depends mainly on the content of organic (mostly petrochemicals) pollutants. The dependence of the samples' COD on the added amounts of the adsorbents is shown in Fig. 3. In this case, the performance of the adsorbents mixture is also better than that of the individual components.

As seen from Fig 2 and 3, a 4:1 composition of coal refining sludge and technical pyrocarbon is more effective than the individual components. Therefore this composition should be used in water-cleaning cartridges.

It is more convenient to realize any adsorption cleaning technology in a dynamic mode when the wastewater to be treated is collected in some kind of pond and then is discharged continuously through the water cleaning equipment than to do that in a static mode when the wastewater is poured in some technological tank, treated, and then discharged.

Results of the flow decontamination of water are shown in Table 2. They embrace only the first three liters because no changes in the water absorbance and COD were determined after passing three liters through the filtration cartridge. It can be seen that this water cleaning method is effective in the elimination of petrochemical water pollution agents. COD decreases by eight times, and absorbance drops by six times. It means that about 85% of the petrochemical pollution is extracted from treated wastewater.

The water decontamination performance of the cartridges slightly degrades as wastewater passes through – mostly in the context of COD. However, within the amount of water used in this investigation, this degradation is not crucial and does not exceed 10% of the initial water cleaning effectiveness. The suspended particle elimination ratio remains almost stable. This parameter depends mostly on the mechanical fixation of the suspended pollution inside the adsorbent layer, which has a much higher filtration capacity than its adsorption capacity, which is important for the elimination of dissolved petrochemicals.

Since the maximum adsorption capacity of petrochemicals on the mixed adsorbent reported in [6] is 0.15 kg/kg, and taking into account that an average daily drainage/wastewater discharge of such car filling/service facility is about 1000 L, it can be seen that 30000 L of the monthly-formed wastewater consisting of 0.09% of petrochemicals will bring about 27 kg of petrochemical pollution agents to be adsorbed. Taking into account its adsorption capacity (see above), it is obvious that such an amount of pollutants requires only about 4 kg of the adsorbent mixture per month. Therefore, a small pond or underground tank can be established to collect the technological wash-offs and drainage/wastewater from a typical CFS. It should be equipped with a filtration cartridge filled with 4 kg of the mixed adsorbent. Filtration of the water with a flow rate of not more than 1 L/min ensures extraction of mixed suspended particles and organic pollutants, which leads to an 85% decrease in the COD. The expected operation time before cartridge replacement is not shorter than one month.

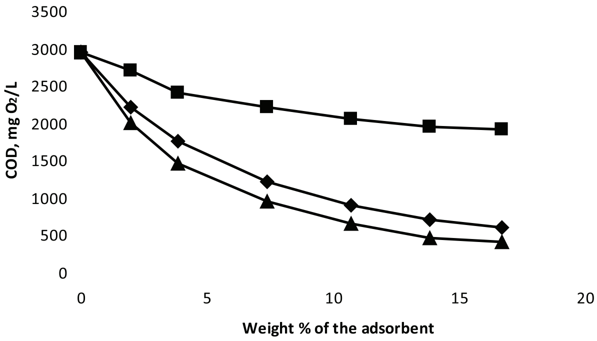

Fig. 3. The dependence of the samples' COD on the added amount of various adsorbents. ◆ – coal refining sludge; ■ – technical pyrocarbon; ▲ – 4:1 mixture of the sludge and pyrocarbon

Rys. 3. Zależność ChZT próbek od ilości dodanych różnych adsorbentów. ◆ – szlam z rafinacji węgla; ■ – pirocarbon techniczny; ▲ – mieszanina 4:1 szlamu i pirocarbonu

Tab. 2. Effectiveness of wastewater treatment by the coal sludge/pyrocarbon cartridges

Tab. 2. Skuteczność oczyszczania ścieków przez wkłady z mułu węglowego i węglowodorów ropopochodnych

Adsorbing mixture	Absorbance				COD, mg O_2/L			
	Raw water	1 L	2 L	3 L	Raw water	1 L	2 L	3 L
Coal sludge/pyrocarbon	1.2	0.2	0.21	0.21	3250	420	440	450

Conclusion

A 4:1 mixture of the "T" brand coal refining sludge and technical pyrocarbon proved its effectiveness in the decontamination of wastewater from petrochemical pollutants and mixed mechanical suspensions. Up to 85% of petrochemicals can be extracted from the aqueous phase by filtration of the regular car filling/service station's wastewater through a cartridge filled with this mixture. The water decontamination performance of a cartridge filled with 4 kg of adsorbing mixture should remain sufficient for at least one month. Then the waste adsorbent can be utilized by adding to the solid coal-based fuel mixtures for thermal power stations or other similar facilities.

This ecofriendly solution requires only solid industrial waste materials allowing an enhancement of the water quality condition in the small urban rivers often suffering from the low-tonnage and numerous uncontrolled discharges of drainage/wastewater from car filling/washing/service stations and other similar service points.

Literatura – References

1. Igor Winkler. Small urban rivers of Chernivtsi: Level of organic pollutants content, main sources and effective green solutions. In: NATO advanced workshop "Dangerous pollutants (xenobiotics) in urban water cycle". Proceedings (2-6 May 2007). Lednice, Vensen, 2007. 45-50. DOI: 10.1007/978-1-4020-6795-2
2. Feng-Jiao Peng, et al. Occurrence and ecological risk assessment of emerging organic chemicals in urban rivers: Guangzhou as a case study in China. Science of the Total Environment, 2017. 589: 46-55. DOI: 10.1016/j.scitotenv.2017.02.200
3. J. Wang, X. D. Liu, J. Lu. Urban river pollution control and remediation. Procedia environmental sciences, 2012. 13: 1856-1862. DOI: 10.1016/j.proenv.2012.01.179
4. M. Jamal Uddin, Yeon-Koo Jeong. Urban river pollution in Bangladesh during last 40 years: potential public health and ecological risk, present policy, and future prospects toward smart water management. Heliyon, 2021. 7: 1-23. DOI: 0.1016/j.heliyon.2021.e06107
5. Peng Zhang, et al. Chemodiversity of water-extractable organic matter in sediment columns of a polluted urban river in South China. Science of the Total Environment, 2021. 777: 146127. DOI: 10.1016/j.scitotenv.2021.146127
6. Mariya Fedoryak et al. Adsorption of the petrochemical pollutants released at the small vehicle-service facilities on the coal refinery sludge/pyrocarbon compositions. Inżynieria Mineralna – Journal of the Polish Mineral Engineering Society, 2021. 47: 61 – 66. DOI: 10.29227/IM-2021-01-08
7. Igor Winkler, Volodymyr Diychuk. Adsorption of toluene from the mixed water–toluene system on medicinal activated carbon. Canadian Journal of Chemistry, 2014. 92: 392-396. DOI: 10.1139/cjc-2014-0030
8. Igor Winkler and Anna Saviuc. Adsorption and electroadsorption of toluene on some graphite/clay materials. Revue Roumaine de Chimie, 2016. 61: 773-778
9. Marwa Elkady, Shokry Hassan, and Hamad Hesham. New activated carbon from mine coal for adsorption of dye in simulated water or multiple heavy metals in real wastewater. Materials, 2020. 13: 2498-2503. DOI: doi.org/10.3390/ma13112498
10. Sepher Sadighi, Alivand Sheikh Masood, and Faghihi Morteza. Selection of adsorbents for different applications and processes: A Review. Petroleum & Coal, 2019. 61: 932-948
11. A. S. Makarov, et al. Utilization of industrial wastewater in production of coal-water fuel. Journal of water chemistry and technology, 2014. 36: 180–183
12. Igor Winkler and Anna Saviuc. Diffusive and kinetics control of the liquid phase adsorption of toluene of some graphite/clay compositions and pure graphite. Revue Roumaine de Chimie, 2018. 63: 1169-1174

Skuteczność niektórych kompozycji mineralnych na bazie węgla w dekontaminacji i ochronie środowiska wód małych rzek miejskich

Zbadano skuteczność szlamu z przeróbki węgla marki "T", pirocarbonu technicznego i ich mieszaniny jako adsorbentów do odkażania wody drenażowej z zanieczyszczeń organicznych. Zanieczyszczone próbki wody zostały pobrane z systemu odwadniającego zwykłej stacji obsługi samochodów, a następnie poddane działaniu adsorbentów. Absorpcja wody i chemiczne zapotrzebowanie tlenu (ChZT) były kontrolowane jako parametry jakości wody i skuteczności dekontaminacji.

Jako najskuteczniejszy adsorbent dla mieszanych zanieczyszczeń petrochemicznych i mechanicznych zastosowano mieszaninę 4:1 szlamu z rafinerii węgla i pirocarbonu technicznego. Stwierdzono, że kompozycja ta skutecznie odkaża wodę z mieszanych zanieczyszczeń organicznych.

Wkłady do oczyszczania wody wypełnione tą kompozycją adsorbentów wykazały wysoką skuteczność odkażania, eliminując około 85% petrochemicznych zanieczyszczeń wody. Wydajność ta nie ulega znacznemu pogorszeniu, a 4 kg adsorbentu powinno wystarczyć do oczyszczenia ilości ścieków powstających na stacji benzynowej przez co najmniej miesiąc.

Słowa kluczowe: *małe rzeki miejskie, woda zanieczyszczona olejem, adsorpcyjne uzdatnianie wody, mieszane adsorbenty węglowe, pirocarbon*