Adsorption of the Petrochemical Pollutants Released at the Small Vehicle-Service Facilities on the Coal Refinery Sludge/Pyrocarbon Compositions

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Abstract

It has been proven that the use of coal-like adsorbents with the mosaic and hydrophobic surface structure is efficient in cleaning the wastewater from a wide range of pollutants under the condition of their uncontrolled release from various small enterprises. This range includes such environmentally dangerous agents as petrochemicals and other pollutants formed at car filling, carwash stations or other similar facilities. Technical pyrocarbon and the coal refinery sludges are readily available waste materials with high porosity, which exhibit some adsorption activity and can be utilized in water/wastewater treatment solutions. Then the adsorbents can be either disposed of at the landfill areas or incinerated as components of some secondary fuels. The highest adsorption performance is achieved for the sorbent mixture of the refinery sludges and technical pyrocarbon with the ratio of the components 4:1.

If the wastewater is flowing through this composition, the degree of petrochemicals removal reaches 75-80% for the mixture sludge/technical pyrocarbon, while the pure pyrocarbon ensures the removal degree of 15-20% only. Though adsorption efficiency under stationary conditions (keeping the adsorbent and the wastewater in contact inside some decontamination pond/vessel for at least 24 h) is higher, this option is hard-to-realize for a small car service/wash station. As an alternative, comparatively small wastewater cleaning cartridges filled with the 4:1 mixture of coal sludge and technical pyrocarbon can be recommended for preliminary decontamination of the wastewater formed at such enterprises before their discharge to the local municipal sewerage lines.

Keywords: *coal refinery waste, pyrocarbon, adsorption efficiency, petrochemicals, pollution, wastewater treatment technologies*

Introduction

Environmental pollution with oil and petrochemical products is one of the most dangerous consequences of human-induced activity. Petrochemical products affect human and animal bodies, water plants, physical, chemical and biological condition of the water objects. The maximum possible concentration (MPC) of petrochemical products in the household and drinking waters in Ukraine is 0.3 mg/L, and MPC of petrochemical products in the fishery utilization water is limited by 0.05 mg/L [1, 2]. These limitations are quite strict, and it is required to apply various water/wastewater treatment technologies to remove or decontaminate the petrochemical pollutions of water and bring its quality parameters within these limits. This issue is especially acute since many carwash, filling and service stations usually discharge their wastewater into the local municipal sewerage without any special treatment. As a rule, this wastewater is severely contaminated with various petrochemicals coming from the vehicle oils, grease, corrosion protection materials, spills of fuel and other liquids, and other similar sources [3-5].

An ordinary carwash produces an average of 0.7 ÷ 1.2 m^3 of wastewater a day. Such wastewater contains about 800 ÷ 3000 mg/L of suspended substances and 500 ÷ 900 mg/L of petrochemical products [3, 4]. The car filling stations discharge a lesser amount of wastewaters but with much higher pollution [6].

A wide variety of methods and technologies or their combinations is applied for reuse, reclamation and cleaning of these wastewaters: regular filtration, chemical, photo- or electro-oxidation, various kinds of adsorption, extraction, biotreatment, and others [7, 8].

Adsorption is one of the highly effective wastewater cleaning methods. Previously it has been established that graphite or activated charcoal is a more effective adsorbent for some petrochemicals than inorganic clays or silica gel [9, 10]. It has also been found that the process of toluene adsorption on graphite or activated charcoal materials occurs according to the mixed kinetic/diffusion control mechanism [11]. However, the efficiency of the adsorption of various petrochemical compounds can vary within significant limits [12]. Carbon nanotubes have shown even better efficiency in petrochemicals adsorption [13], but this material is still quite expensive while various pyrocarbons are abundant and readily available at a comparatively low price. The same is true for the coal sludges usually collected as waste or by-product at the coal refinery plants.

From a competitive point of view, it is important to keep the treatment process easy and relatively cheap, making the introduction of such technologies feasible for small companies. Thus, mobile and replaceable wastewater treatment modules are reasonable for extraction of the relatively low amounts of wastewaters formed at the low-tonnage pollution discharging points before their release to the sewage.

Considering the physical and chemical characteristics of the oil products and following the abovementioned results of the previous investigations, it is expected that the adsorbents with the hydrophobic surface should be the most efficient for such treatment technologies.

Pyrocarbon or semi-cake is a hydrophobic material obtained as the solid residue in the pyrolysis of various non-compostable polymer and rubber wastes. It is cheap,

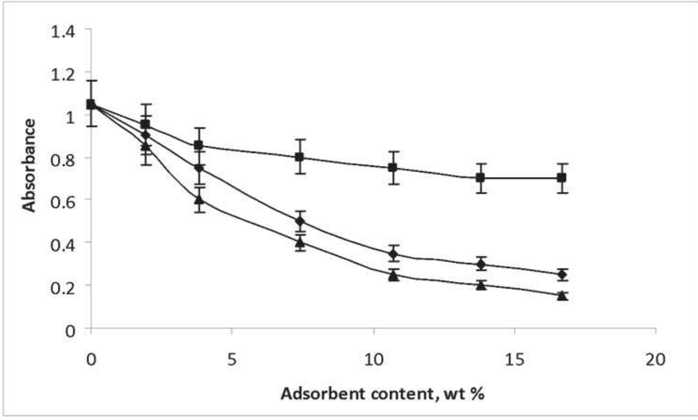

Fig. 1. Dependence of the wastewater absorbance on the adsorbent concentration in the case of 'static' (see explanations in the text) treatment conditions: (▪) – pyrocarbon; (◆) – coal sludge; (Δ) 4:1 mixture of the sludge and pyrocarbon. Vertical bars show the relative experimental ranges for each experimental series.

Rys. 1. Zależność absorbancji ścieków od stężenia adsorbentu w przypadku „statycznych" (zob. wyjaśnienia w tekście) warunków oczyszczania: (▪) - karbonizat; (◆) - muł węglowy; (Δ) 4:1 mieszanina szlamu i karbonizat. Pionowe słupki pokazują względne zakresy eksperymentalne dla każdej serii eksperymentalnej.

highly porous and can be used in numerous technological applications as a secondary fuel or charcoal substitute.

Some admixture of the sludge (a by-product of coal refining) can also be used as a cheap component of the adsorbent composition. However, it should be clarified how this component will influence the adsorption efficiency of pyrocarbon.

In this work, a comparative efficiency of pyrocarbon, coal sludge and the pyrocarbon/sludge composition has been investigated in the adsorption of petrochemical mixtures using absorbance or the chemical oxygen demand (COD) index as a method of determination of the total concentration of petrochemicals in water.

Materials and experimental methods

Wastewater samples were collected from a conventional carwash station in Chernivtsi, Ukraine. They were taken from an accumulation tank where the untreated wastewater is collected before being discharged to the municipal sewerage.

The following materials were tested as adsorbents:

1. Coal refinery sludge of the T-brand coals obtained at Kondratyevska Central Mining and Processing Enterprise, Ukraine. The material humidity is 15.0% and the ash content is 43.1%.
2. Technical pyrocarbon obtained after the pyrolysis of various unsorted polymer wastes. The material humidity is <1% while the ash content is about 29.5%.
3. A mixture of the sludge and pyrocarbon with the mass ratio 4:1

It has been found previously [14] that this ratio of the components ensures the highest anti-sedimentation stability because highly dispersed pyrocarbon particles form the mixed contact aggregates with the sludge preventing them from being washed out. Therefore, it is expected that this composition would exhibit the highest anti-agglomeration stability, the easiest access to the entire surface of the particles and the best adsorption performance. That is why it was used as another adsorbent.

All samples of the adsorbent were ground using the ball grinder. Then the 0.5-50 μm fractions of each adsorbent were separated using the appropriate sieves and used in the experiments.

The following physical and chemical characteristics of the wastewater were determined: optical density (absorbance) and chemical oxygen demand (COD). These parameters are important for the understanding of the degree of water contamination with suspended particles and the chemically oxidizable compounds (mostly organic petrochemicals). Further, these parameters were used to evaluate an efficiency of the adsorbents.

An approximate COD of the samples was determined according to the simplified procedure [15]: 5 mL of the filtered sewage water were mixed with 5 mL of the 0.1 N solution of potassium dichromate in the 250 mL conical flask, and then 15 mL of the concentrated sulfuric acid were added gradually at the constant stirring. Then 50 mL of the distilled water were added, and the mixture was heated up to the boiling point and kept 2 h at this temperature. After cooling down to room temperature, the sample was titrated by the 0.1 N solution of the Mohr's salt $FeSO_4*(NH_4)_2SO_4*6H_2O$ against the redox indicator ferroin until the distinct change in the indicator color from blue-green to reddish. Same manipulations were done simultaneously with the control probe consisting of distilled water instead of the sewage water.

COD value was calculated by the formula:

$COD = 8*(V_0 – V) * 0.1 /A$, where V_0 and V are the volumes of the Mohr's salt solution spent for titration of the control and test samples (mL); 0.1 – the Mohr's salt solution normality; 8 – the oxygen equivalent; A – the volume of the test sample taken for the analysis (mL).

The absorbance of the samples was determined by the photoelectric colorimeter KFK-2 by LOMO at the wavelength λ = 540 nm [5].

Adsorption efficiency was evaluated either under the static conditions (some amount of the adsorbent was added to the sewage water) or under the dynamic conditions (sewage water was pumped through the adsorbent bed).

When evaluating the static adsorption efficiency, some adsorbent (0.5-17 g) was added to 25 mL of the sewage water.

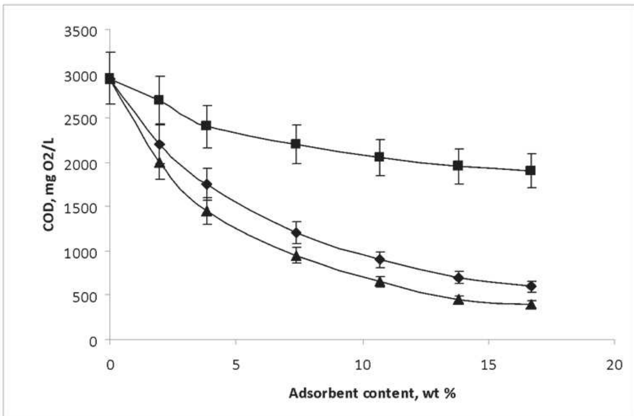

Fig. 2. Dependence of the wastewater COD (mgO_2/L) in the case of 'static' (see explanations in the text) treatment conditions: (▪) – pyrocarbon; (♦) – coal sludge; (Δ) 4:1 mixture of the sludge and pyrocarbon. Vertical bars show the relative experimental ranges for each experimental series.

Rys. 2. Zależność ChZT ścieków (mgO_2/L) w przypadku „statycznych" (patrz wyjaśnienia w tekście) warunków oczyszczania: (▪) - karbonizat; (♦) - muł węglowy; (Δ) 4:1 mieszanina szlamu i karbonizatu. Pionowe słupki pokazują względne zakresy eksperymentalne dla każdej serii eksperymentalnej.

The mixture was stirred and left for 24 hours, then filtered through the "Red Tape" filter paper, and the filtrate was used in the follow-up investigations. The control test with the distilled water sample was processed by the same procedure simultaneously. An amount of the added adsorbent was limited by 17 g because, according to the experimental data, a dependence of the adsorption efficiency on the adsorbent amount reached its limit value (the dependence line slope turned practically horizontal – see Fig. 1 and 2) when this amount was close to 15 g. Therefore, further addition of the adsorbent was not reasonable as it would not cause any noticeable progress in the wastewater decontamination.

When evaluating the dynamic adsorption efficiency, a porous fabric was placed in the Buchner's funnel (diameter 8 cm), a 25 g sample of the adsorbent was poured into the funnel and covered with another porous fabric. The funnel was installed in the Bunsen's flask, and then the sewage water was vacuum filtered through the funnel. The constant vacuum of 0.3 atm produced by the electric vacuum pump was applied in all the experiments throughout this series.

Results and Discussion

Obviously, the more adsorbent added, the more petrochemicals can be captured and removed from the system. However, when present in the water-based system, the petrochemicals form two phases – the surface film and the bulk phase.

Coal sludge is a material that consists of two phases: the hydrophobic (the coal-like components) and the hydrophilic (mineral components) ones. That is why its wettability is comparatively high and its adsorption efficiency reaches 80% (see the dependence of the system's absorbance in Fig. 1). On the other hand, the sludge particles do not float and, therefore, if not stirred, the adsorption process occurs mostly in the bulk and does not involve the surface film.

Pyrocarbon, in contrary, is mostly hydrophobic material that is not wettable and, consequently, in case of using this adsorbent, the process involves mostly the surface film leaving the bulk pollutants intact. As a result its efficiency is lower and reaches only 15-20% (see Fig. 1).

The 4:1 mixture of the above components ensures the most efficient removal of the petrochemicals both from the surface layer and the bulk of the system and the overall decontamination ratio, in this case, reaches 85-90% (see Fig. 1). As seen from Fig. 1, the wastewater absorbance decreases from 1.05 to 0.15 after adsorption by the 4:1 adsorbents mixture. This change corresponds to an 85% decrease in the concentration of the optically active water pollutants.

Similar tendencies have been registered for the wastewater COD after its treatment with the three types of the adsorbents (see Fig. 2).

It should be understood that practical realization of this static water treatment scheme would require a specialized water treatment/decontamination pond that can hardly be put in practice in the case of a small car-washing station or any similar enterprise.

That is why the efficiency of a more feasible dynamic water treatment approach has been investigated at the next stage of this work. According to this approach, the contaminated water or wastewater must be pumped through a relatively small cartridge filled with the adsorbent. This approach is less material, energy, and resources demanding and seems quite feasible even at a small-size car service or washing station.

The 4:1 mixture ensures the best adsorption efficiency, followed by the sludge and then pyrocarbon (see Table 1). In the latter case, the adsorption takes place within the surface layer only. Usually, the petrochemicals stay mostly on the surface and, taking into account this fact, the "surface" efficiency of pyrocarbon seems unexpectedly low. However, it should be understood that the detergents are used in the regular operation of car wash stations, and therefore there are considerable amounts of detergents present in the wastewater. They promote better emulsification of pyrocarbons with water and increase the bulk concentration of this pollutant, which is not affected by the purification with pyrocarbon. That is why the performance of this adsorbent is noticeably worse than for the other two materials.

At the next stage, the efficiency of the dynamic purification of wastewater was investigated. 1, 2 or 3 liters of wastewater were used in this experiment (see further details related to the experimental procedure above, in "Materials and Experimental Methods"). The initial COD of the wastewater samples was 3000 mg O_2/L, and the absorbance was 1.05. The same

Tab. 1. Some water quality parameters of the wastewater samples after passing through the adsorbent layer

Tab. 1. Wybrane parametry próbek ścieków po przejściu przez warstwę adsornbenta

Adsorbent	Absorbance			COD, mg O_2/L		
	1 L	2 L	3 L	1 L	2 L	3 L
Sludge	0.32	0.32	0.33	650	650	680
Pyrocarbon	0.65	0.67	0.7	1900	1950	1950
Sorbents mixture	0.2	0,21	0,21	420	440	450

parameters are given in Table 1 for the samples after they were treated with different sorbents.

It can be seen that the sorbents mixture remains the most efficient adsorbent, followed by the sludge and then – pyrocarbon. The dynamic adsorption efficiencies with the use of coal slacks and sorbent mixture are close to those in the static conditions (maximum efficiency also reaches 75-80 %). Some insignificant decrease in the dynamic efficiency is caused by a lesser contacting time between the contaminated water and the adsorbent resulting in incomplete adsorption of the petrochemicals.

However, in the dynamic treatment, the pyrocarbon efficiency is noticeably higher than that for the static conditions. In our opinion, this is caused by the fact that pyrocarbon is fixed between two porous layers having the wastewater flux flowing through this bed. Under such conditions, pyrocarbon cannot float, and the entire water phase contacts with the sorbent surface, improving the degree of water purification as compared with that in the static conditions when pyrocarbon interacts within the surface layer only. Nevertheless, pyrocarbon, an extremely hydrophobic material, remains the worst adsorbent among the materials involved in this investigation.

It should also be emphasized that all adsorbents mentioned above can easily be utilized after their use as adsorbents for the petrochemical pollutanrs. There are many options for reuse of such materials as the components of secondary fuel [16]. In this case, they can be incinerated in specially designed water heaters, and the captured petrochemical would only increase their heat productivity.

Conclusion

Coal sludges, technical; pyrocarbon and the 4:1 mixture of these components can be used as efficient adsorbents in the wastewater treatment solutions for small car wash, service and filling stations. A reliable technology involving simple cartridges loaded with the 4:1 components mixture can ensure the purification of the technological wastewaters before the discharge to a local sewerage system. The petrochemicals extraction efficiency reaches 75-80 %, although an issue of the effective operation limits still has to be investigated for different cartridge designs and adsorbent loads.

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Adsorpcja zanieczyszczeń petrochemicznych uwalnianych w małych obiektach serwisowych pojazdów na kompozycje osadu węglowego/pirowęglowego

Wykazano, że zastosowanie adsorbentów węglopochodnych o mozaikowej, hydrofobowej strukturze powierzchni skutecznie oczyszcza ścieki z szerokiej gamy zanieczyszczeń. Adsorbowane są niebezpieczne dla środowiska substancje takie jak produkty petrochemiczne i inne zanieczyszczenia powstające na stacjach paliw, myjniach samochodowych lub innych podobnych obiektach. Techniczny karbonizat węglowy i szlamy z rafinerii węgla są łatwo dostępnymi materiałami odpadowymi o wysokiej porowatości, które wykazują pewną aktywność adsorpcyjną i mogą być wykorzystywane do oczyszczania wody/ścieków. Następnie adsorbenty mogą być albo składowane na składowiskach odpadów, albo spalane jako składniki niektórych paliw wtórnych. Najwyższą wydajność adsorpcji uzyskuje się dla mieszaniny sorbentów z osadów rafineryjnych i karbonizatu technicznego o stosunku składników 4:1. Jeżeli ścieki przepływają przez tę kompozycję, stopień usunięcia petrochemikaliów osiąga 75-80% dla mieszaniny osad/karbonizat techniczny, podczas gdy czysty karbonizat zapewnia stopień usunięcia tylko 15-20%. Chociaż wydajność adsorpcji w warunkach stacjonarnych (utrzymywanie adsorbentu i ścieków w kontakcie w naczyniu dekontaminacyjnym przez co najmniej 24 godziny) jest wyższa, ta opcja jest trudna do zrealizowania w przypadku małych stacji obsługi/myjni samochodowych. Jako alternatywę można polecić stosunkowo niewielkie wkłady do oczyszczania ścieków wypełnione mieszaniną mułu węglowego 4:1 i technicznego karbonizatu do wstępnego odkażania powstających w tego typu przedsiębiorstwach ścieków przed ich odprowadzeniem do lokalnych miejskich sieci kanalizacyjnych.

Słowa kluczowe: *odpady z rafinerii węgla, karbonizat, efektywność adsorpcji, petrochemia, zanieczyszczenia, technologie oczyszczania ścieków*