Lab-scale investigation on remediation of sediments contaminated with hydrocarbons by using super-expanded graphite.

Masi S.[1], Calace S.[1], Mazzone G.[1], Caivano M.[1], Buchicchio A.[1], Pascale S.[1], Bianco G.[2], Caniani D.[1]*

1Università della Basilicata, Scuola di Ingegneria, Viale dell'Ateneo Lucano 10 - Potenza, Italy

2 Università della Basilicata, Dipartimento di Scienze, Viale dell'Ateneo Lucano 10 - Potenza, Italy

*corresponding author: Donatella Caniani

e-mail: donatella.caniani@unibas.it

Abstract

In view of necessity to develop simple, rapid, and efficient methods for monitoring and removal contaminants from soil, a new graphene-based material is presented for treatment of hydrocarbon-contaminated soils. Lab-scale experiments on three soil matrices featured by increasing granulometry were carried to evaluate graphene adsorption capability, as removal efficiency. Soil samples, firstly contaminated with different quantities of mineral exhausted oil up to final concentrations of 12500, 25000, 50000 $mgkg^{-1}$, respectively, were treated with opportune amount of graphene. Results show as the removal efficiency of graphene is directly proportional to contamination level of the soil. Particularly, the best removal efficiency (87.04%) was reached during treatment of gravel samples at maximum contamination level using the highest dosage of graphene, even though good results (80.83%) were also achieved using lower graphene/pollutant ratio. Moreover, graphene at ratio 1/10 showed worse removal efficiencies in treating sea (81.17%) and silica sand (63.52%) than gravel. In this study, also the thermal regeneration was investigated in order to evaluate a possible reuse of graphene with subsequent technical and economic advantages. Graphene-technique proves to be technologically and economically competitive with other currently used technologies, revealing the best choice for the remediation of hydrocarbon-contaminated soils.

Keywords: contaminated sediments, hydrocarbons, remediation, super-expanded graphite

1. Introduction

In the last century, the industrial development has led to spread of wealth, contributing to environmental pollution. In Europe, three million potentially contaminated sites have been counted, of which 10% (300,000 sites) need remediation (EEA, 2015). There are a lot of pollutant agents resulting from the production and use of synthetic products, but only after decades their dangerousness has been acknowledged. Particularly, petroleum products represent more than 50% of soil contaminants (EEA, 2015). Hydrocarbons pollution of soil and water is usually due to accidental spills, losses from tanks or pipelines, mismanagement of storage sites or landfills for industrial waste. The soil pollution represents a critical issue for technicians and researchers because of its difficulty of treatment. In view of necessity to develop simple, rapid, and efficient methods for monitoring and removal these contaminants from soil, a broad spectrum of technologies is available to remove or to degrade hydrocarbons. In this paper, a lab-scale experimentation was carried out to remove hydrocarbons from contaminated soils, using super-expanded graphite as innovative material characterized by high specific surface and adsorption capacity (Zhu *et al*., 2010). To our knowledge, the use of graphene in soil remediation is not enough investigated in the scientific literature. Therefore, to enlarge the available literature on soil and water remediation, laboratory tests were performed, to evaluate the maximum adsorption capacity in several experimental conditions (i.e., granulometry, graphene/pollutant ratio, contact time, and pollutant concentration). The main objective of this work is to treat different types of solid matrix, artificially contaminated with exhausted lubricating oil, using super-expanded graphite as adsorbent. The aim is to achieve high levels of removal by means of reduced quantities of graphite. In this way, it is possible to introduce a new remediation technology which is technologically and economically competitive.

2. Materials and methods

2.1. Properties of graphene

The promising applications of super-expanded graphite arise from its particular structural properties. Graphene is a nanomaterial mainly used to treat water contaminated with hydrocarbons, producing excellent results (Wang *et al*., 2013; Mehdinia *et al*., 2015). Particularly, it is an innovative material with elevated transparency and a large specific surface area (2630 m^2g^{-1}). Moreover, the mechanical resistance is 200 times greater than steel, the flexibility is comparable to that of rubber, the thermal conductivity is twice than that of diamond, the electrical conductivity is higher to any other material and the apparent density is from 2.3 to 9 gl^{-1}.

2.2. Contamination procedure and sample preparation

Sea sand (0.125-0.250 mm), silica sand (1 mm-3 mm), and gravel (2-4 mm) were used to simulate a real contamination during lab-scale tests. 100 g of soil samples, dried in oven at 75°C up to constant weight, were contaminated with exhausted lubricating oil at three different concentrations (i.e. 50000 $mgkg^{-1}$, 25000 $mgkg^{-1}$, 12500 $mgkg^{-1}$). Then, the soil and oil were mixed for 2 minutes in order to obtain homogeneous contaminated samples. Finally, samples were left to rest for 30 minutes, in order to ensure oil adsorption.

2.3 Treatment process description

The physical process, used to remove the contaminant from the mixture (i.e. soil and exhausted lubricating oil), was the adsorption with super-expanded graphite after 30 minutes of rest. The dosage of adsorbent material, as graphene/pollutant ratio, was 1/10, 1/20, and 1/40 for the three contaminated samples, respectively. Graphene was added to the mixture. After suitable magnetic stirring, the soil samples were washed with 500 ml of tap water. The contact times in water were considered as a function of the graphene/pollutant ratio, as shown below:

- t = 2 min → graphene/pollutant = 1/10

- t = 10 min → graphene/pollutant = 1/20

- t = 15 min → graphene/pollutant = 1/40

Therefore, the soil treatment process was a soil washing without surfactants. The soil was removed from the exhaust graphene through gravimetric settling, exploiting the difference in density between the sand and oil-graphene mixture. The filtration was the last step of the treatment process, allowing the separation between the exhaust graphene and the washing water by means of a cloth-like-paper filter.

Therefore, the obtained post-treatment products were reclaimed sand, filter with oil and graphene, and washing water.

2.4. Adsorption measurement

Adsorption capacity of graphene (q) was evaluated as mass of adsorbed pollutant per mass of adsorbent material (mgg^{-1}), following Equation 1 (Petrova *et al*., 2010):

$$q = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where V is the volume of solution, Co and Ce are the initial and the final concentrations of pollutant, respectively, and M is the mass of the adsorbent material. The adsorption capacity represents the capability of graphene to adsorb the oil entrapped in the pores of grains sand, favoring the soil remediation. The efficiency of pollutant removal (E) was also determined as in Equation 2, where C_0 and C_e (mgg^{-1}) are the initial and post-treatment concentrations of pollutant:

$$E(\%) = \frac{(C_0 - C_e)}{C_0} \quad (2)$$

2.5 Reuse of washing water

The soil treatment by means of washing water requires a considerable amount of water, thus the water recirculation is needed to overcome this issue and make the process economically advantageous. Silica sand samples contaminated by exhausted lubricating oil (25000 $mgkg^{-1}$) were treated with super-expanded graphite (1/40 as graphene/pollutant ratio), for 7 cycles and 5 – 10 – 15 – 20 – 30 – 40 – 60 minutes of shaking in water. This process was carried using both clean and recycled water to evaluate the possible difference.

2.6 Regeneration and reuse of graphene

In the present work, possible regeneration processes of super-expanded graphite were investigated to recover and reuse the adsorbent material for subsequent tests. Two graphene samples were regenerated in oven, observing significant pollutant removals by increasing the temperature (360°C, 410°C, 460°C, 605°C) and the time (2h, 4h, 8h, 12h, 24h). The treatment was carried on an oil sample and on a sample with the same amount of oil but with addition of graphene in order to compare the weight loss of the samples after the same treatment time in muffle. The regenerated graphene has been reused (in dosage: 1/100, 1/80, 1/40) to treat water (1l) contaminated with diesel (1 g) to evaluate the adsorption capacity.

3. Results and discussion

3.1 Adsorption of exhausted lubricating oil

The results show different adsorption capacities at different contact times (i.e. 2 min, 10 min, and 15 min) and pollutant concentrations (i.e. 50000 $mgkg^{-1}$, 25000 $mgkg^{-1}$, 12500 $mgkg^{-1}$), as well as at different grain size. Particularly, the maximum adsorption capacity (32332 mgg^{-1}) is achieved during the treatment of gravel sample contaminated with 50000 $mgkg^{-1}$ of oil (Figure 1) after a contact time of 15 min, proving that high removal efficiencies could be reached for sediments with larger grain size. However, at the same contamination condition, an increase is also observed during the treatment of the other samples, reaching values of 21956 mgg^{-1} and 31535.5 mgg^{-1} for sea sand and silica sand, respectively. Generally, low removal efficiencies are recorded during low contact times (i.e. 2 min.), proving the weak adsorption capacity of graphene when the treatment operation conditions are not adequately. Moreover, laboratory tests show how the removal efficiency of graphene increases with pollutant concentration independently of the graphene /pollutant ratio, confirming the reliability of this technique in case of emergency. The sample particle size also affects the treatment because of its strong effect on the removal efficiency and adsorption capacity of graphene. Figure 2 shows the increase of graphene removal efficiency with the increase of particle size of treated sand, reaching the maximum value (83%) during the treatment of gravel at 50000 $mgkg^{-1}$ as contaminant concentration. Finally, it is considered how the variation of graphene/pollutant ratio affects the removal efficiency of the treatment (Figure 3). The maximum removal efficiency value of 77.24 % is obtained, using 1/10 as graphene/pollutant ratio during the remediation process at 50000 $mgkg^{-1}$ as contaminant concentration. However, removal efficiency values of 71.92% and 71.52 % are also achieved using 1/20 and 1/40 as graphene/pollutant ratio, respectively, confirming the excellent efficiency of graphene during the treatment of samples with high contaminant concentrations. The removal efficiency of graphene at different operation conditions is presented in Table 1.

3.2 Reuse of washing water

The removal efficiency obtained using clean and recycled washing water shows comparable values of 57.61% and 51.34%, respectively, at the contact time of 60 minutes. The use of recycled water reduces the removal efficiency because graphene absorbs the oil from both water and soil. To overcame this issue an additional small amount of graphene could be added in order to treat exclusively the washing water.

3.3 Regeneration and reuse of super-expanded graphite

The tests, carried by varying both the temperature and the treatment time, show that during the regeneration of graphene at 460° for 4 hours no graphene losses occur. Indeed, the regeneration treatment not change the graphene characteristics and the weight loss in the oil-graphene mixture is attributed to oil. The comparison between the achieved results using regenerated graphene and those using pure graphene confirms that the use of regenerated graphene appears to be a promising alternative to pure graphene, proving that no changes occur in the adsorption properties of graphene after the regeneration process.

3.4 Economic feasibility of different methodologies for soil remediation

Known 100 € kg^{-1} the cost of super-expanded graphite, the treatment of 100 g of gravel at the maximum contamination (50000 mg kg^{-1}) by means of graphene in ratio 1/20 (0.25 g) costs 0.025 €, achieving 81.14% as removal efficiency. Table 2 shows the treatment costs (€ kg^{-1}) related to the graphene/pollutant ratio, with a minimum of 31.2 € ton^{-1} and a maximum of 500 € ton^{-1}. The economic feasibility of the presented remediation technique is rather complex if compared to classic treatments, because the increase of pollutant and graphene concentrations causes an increase of costs.

However, costs will decline once entered permanently in the market, getting the technique more advantageous.

4. Conclusion

The results of the presented study highlighted the positive aspects of the application of graphene for remediation of soil contaminated with hydrocarbons. The remediation process was carried out in very short time. In fact, the adsorption capacity of the super-expanded graphite achieves values of 20,000 – 30,000 mgg^{-1} for both sea sand and silica sand and 32,000 mg g^{-1} for gravel, respectively, within 15 minutes of contact. This values are very high compared to ones of the adsorbent materials currently used in remediation processes, allowing to treat elevated amounts of material in medium-sized plants. The treatment of soil with higher contaminations (i.e. 50,000 $mgkg^{-1}$) registers removal efficiencies of about 90% - 80% - 60% for gravel, silica sand, and sea sand, respectively, whereas the results tend to decline at lower contaminations (i.e. 25000 - 12500 mg kg^{-1}). For this reason, super-expanded graphite could be used in case of large contaminations, typical of recent accidents and spills. The remediation technique is more efficient for coarse-grained materials (e.g. silica sand and gravel), reaching removal efficiency close to 90%. These results are found to be highly promising, because the removal efficiencies obtained by means of graphene are higher than those obtained by means of activated carbon, considered the best adsorbent material until now (Gong *et al*., 2007; Petrova *et al*., 2010). Therefore, graphene technique can be considered a remediation system with many potentiality, even in case of accidents with elevated contamination. The treatment process which exploiting the adsorption capacity of the super-expanded graphite can be the best choice for the remediation of soil contaminated with hydrocarbons. In fact, thanks to its excellent removal efficiency, it is better than the biological, chemical – physical, and thermal technologies actually in use. Moreover, this innovative nanomaterial ensures good results also in application on solid matrix never studied until now.

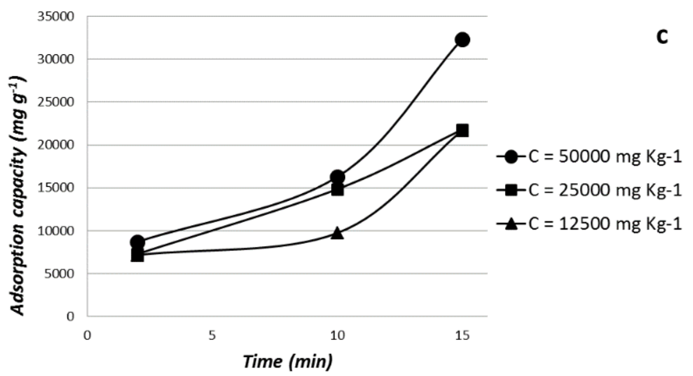

Figure 1. Trends of the adsorption capacity of graphene, as a function of contact time. Conditions: 100 g gravel; exhausted lubricating oil concentrations: (●) 50000 mg kg-1; (■) 25000 mg kg-1; (▲) 12500 mg kg-1; treatment time: 2min; 10min; 15min .

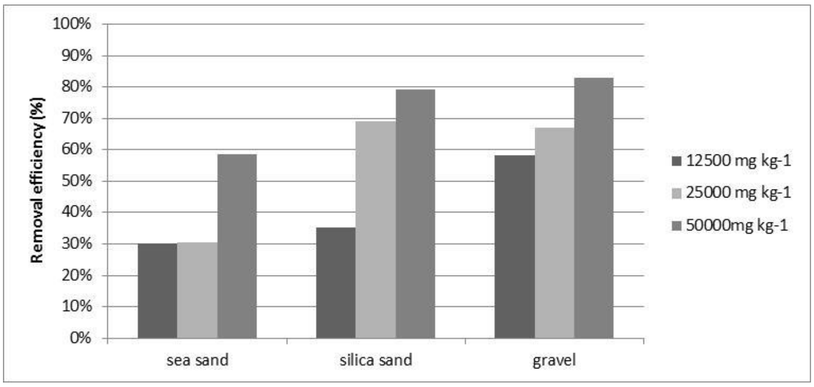

Figure 2. Effect of the particle size on the removal efficiency of graphene. Operation conditions: 100 g sea sand , 100 g silica sand, and 100 g gravel; exhausted lubricating oil concentrations: 12500 mgKg^{-1}; 25000 mgKg^{-1}; 50000 mgKg^{-1}.

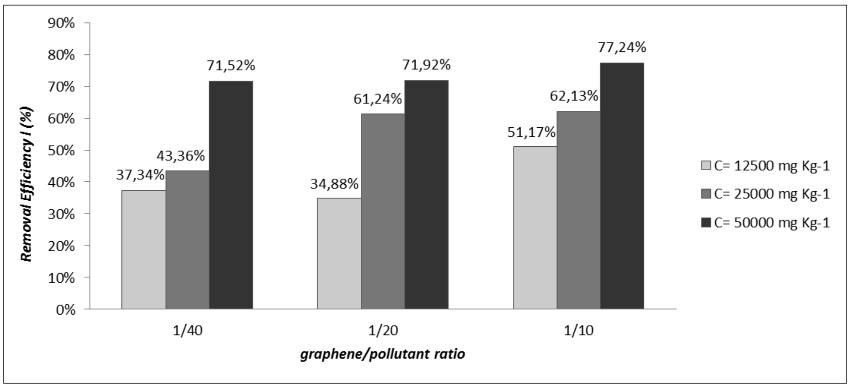

Figure 3. Effect of graphene/pollutant ratio on graphene removal efficiency. Operating conditions: 100g sea sand, 100 g silica sand, and 100 g gravel; graphene/ pollutant ratio: 1/10; 1/20; 1/40; exhausted lubricating oil concentrations: 12500 mgKg^{-1}; 25000 mgKg^{-1}; 50000 mgKg^{-1}.

Table 1. Removal efficiency of graphene in different operating conditions: graphene/pollutant ratio 1/10 – 1/20 – 1/40; exhausted lubricating oil concentrations: 12500mgKg^{-1}; 25000 mg Kg^{-1}; 50000 mg Kg^{-1}.

CONTAMINATION (mg kg^{-1})	GRAPHENE/POLLUTANT RATIO	REMOVAL EFFICIENCY (%)		
		SEA SAND	*SILICA SAND*	*GRAVEL*
50000	1/10	**63.52%**	**81.17%**	**87.04%**
	1/20	57.22%	77.40%	81.14%
	1/40	54.89%	78.84%	80.83%
25000	1/10	36.22%	77.31%	72.86%
	1/20	38.90%	70.77%	74.04%
	1/40	16.37%	59.27%	54.44%
12500	1/10	37.91%	43.92%	71.68%
	1/20	20.71%	35.56%	48.38%
	1/40	32.10%	25.72%	54.20%

Table 2. Graphene / pollutant ratio and costs for the investigated treatments.

*Concentration (m*g kg^{-1}*)*	*graphene /pollutant Ratio*			*Cost (€ kg^{-1})*		
	1/10	1/20	1/40	1/10	1/20	1/40
50000	5 g	2.5 g	1.25 g	0.5	0.25	0.125
25000	2.5 g	1.25 g	0.625 g	0.25	0.125	0.0625
12500	1.25 g	0.625 g	0.312 g	0.125	0.0625	0.0312

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