*Al-Azhar Bulletin of Science Vol. 30, No. 2, (December) 2019, pp. 13-18*

# APPLICATION OF GAMMA RADIATION FOR REMEDIATION OF PETROLEUM CONTAMINATION FROM SOME REFINERIES IN THE VICINITY OF SUEZ GULF

**Nabila A. Ali[1], Omayma E. Ahmed[2] and Saleh M. Abdou[3]***

*(1) Suez Oil Processing Company, Suez, Egypt*
*(2) Egyptian Petroleum Research Institute, Nasr City, P.O. 11727, Cairo, Egypt.*
*(3) Atomic Energy Authority(AEA),National Centre for Radiation Research & Technology, Cairo, Egypt*
* Corresponding author: salehabdou03@yahoo.com

## ABSTRACT

Suez Gulf has been affected by the discharged pollutants. The concentration of adsorbed poly-aromatic hydrocarbons (PAHs) in aquatic sediment is an appropriate index of the status of pollutants in the marine environment. Sediment samples were collected from five sites covers 2.5 km at equal distances along the outlets of the discharge basins of some petroleum refineries in the vicinity of Suez Gulf. The concentrations of (PAHs) were determined via HPLC analysis. The concentrations in sediments in the five sites varied between 22333.983±102 and 73597.864±187 ng/g dry weights with 43016.278±149 ng/g dry weights as the average concentration. Gamma irradiation of the polluted samples were performed and compared with the non-irradiated polluted samples, the changes in the PAHs concentrations were observed. The remediation of toxic pollutants of PAHs as petroleum residues by Gamma radiation has been observed. So the influence of applied dose on the degradation of PAHs concentrations in sediment samples has been studied. The results indicate that, the concentration of PAHs in the irradiated samples of sediments ranged between 16.231±3.7 and 188.531±12.2 ng/g dry weights with 82.184±7.3 ng/g dry weights as the average concentration. Which means that the gamma radiation has a high effect on the PAHs pollution. The variation in the concentrations of the PAHs in the extracted oils with the gamma irradiation followed by HPLC analyses, is investigated.

**Keywords**: PAHs, Gamma radiation, HPLC, Remediation, Adsorption; Polluted sediment

## INTRODUCTION

The current work evaluates the concentrations of the PAHs and the origins of contamination (pyrolytic or petro-genic) of the sediment samples along the outlets of the discharge basins of some refineries in the Vicinity of Suez Gulf. Also, studying the possibility of remediation of the PAHs pollution using gamma irradiation is investigated.

Marine Pollution (mainly from untreated industrial wastes) is a common marine environmental issue in the Suez Gulf region, whereas the petroleum pollution is more intense in the Vicinity of Suez Gulf. Other sea based sources of pollution in the area are the hazards of the production accidents and spills as the discharge of oily wastes correlated with the offshore oil operations and activities [1].

PAHs are organic materials comprised with at least two aromatic rings, which might be formed during the fragmented pyrolysis of petroleum products, wood and yield deposits, procedures of the thermal evolution of sedimentary organic matter and through biological synthesis [2,3,4].

Anthropogenic activities, such as wet or dry atmospheric deposition, discharges of domestic effluents and industrial, maritime transport and by-product spills are considered the major resources of PAHs discharged to the environment [5,6].

The oily wastes are considered the most sinks of PAHs in marine environments. In this manner, for the evaluation of the PAHs in coastal ecosystems, many environmental studies have investigated [7,8,9,10].

High concentrations of PAHs in the Selangor River and the estuarine areas were associated in Malaysia with domestic effluent discharge, urban densification and intensive industrial activities [11]. In the marine zones of San Diego Bay, high concentrations of PAHs were reported [12]. Also, in Egypt, the

Mediterranean coastal environment the concentrations of the PAHs in the sediments was studied. It announced higher concentrations of PAHs at regions under anthropic influence, for example, urban areas, shipyards, industrial and docks [13].

Many surveys are executed on the characteristics of poly aromatic hydrocarbons, their potential to manifest the eco-toxicological activity, high stability, additionally their tendency to adsorb to the suspended material and accumulate in sediments [14]. The presence of these pollutants in Gulf water and sediments are toxic and hard to be completely degraded [15].

In a particular sample, the constituents of PAHs generally give consideration to the sources producing PAHs. Pyrogenic, petrogenic, and biogenic are the three major types of PAHs that vary according to their genesis[16,17,18].

The application of ionizing radiation to minimize the concentration of PAHs in industrial effluents has significant environmental and technical advantages compared to chemical, biological and physical procedures. Such clean technique has ever left any residue [19]. It degrades the organic compositions, creating easily biodegradable materials. The PAHs submissive to the photodegradation due to their sensibility to electromagnetic radiation: ultraviolet and gamma radiation [20]. Photo degradation and oxidation and their combination are therefore considered to be the most effective methods for PAH destruction [21].

## 2. MATERIALS AND METHODS

High performance liquid chromatography (HPLC) auto Sampler 616 Plus water HPLC 600 with Dual Absorbance Detector 2487 analysis was used in the PAH identification and quantification in the extracted oil. The HPLC condition: the column used was Supelcosil LC-PAHs 15 cm, 4.6 mm ID, UV type, 254 mm detector, the sample volume was 100 μL and the flow rate was 1.2 ml/min. Before use in the current procedures, the solvents were redistilled. The reagents were chemically pure or analytical reagent grade.

Samples were collected from five sites covers 2.5 km at equal distances along discharge basins of some petroleum refineries in the vicinity of Suez Gulf. Each site covers (500 meter) five stations at equal distances (100 m), then mixed and stored in precleaned jars, allowing to interests in each site and distance.

Extraction of petroleum oil from sediment samples of about 500 g. The extract was filtered through anhydrous sodium sulfate and the sample volume was reduced to about 0.5 ml. The samples were transferred quantitively to glass vials. The extracted sample oil was concentrated to approximately 0.2 ml using dry nitrogen. The oils-extracted from surface sediment samples were analyzed.

The irradiation process of the PAHs samples was carried out at the dose rate of 1.9 kGy/h at room temperature by means of CO-60 gamma source “4000 A, Indian gamma chamber”. The samples were irradiated to gamma irradiation dose of 20 kGy.

## 3. RESULTS AND DISCUSSION

### 3.1. Occurrence and concentration of the PAHs in polluted sediments

According to the industrial effluents and different processes of the petroleum refineries there are high rate of oily wastes drained to the water stream of the Gulf and the shore sediments after treatment. Actually the program of treatment cannot remove all the residual concentrations of oil from the drained wastewater. So, the outlets of wastewater in most of the time include residual concentrations of oil, which accumulate in sediment and water.

So, the current work was aimed to assess the possible origins of 16 PAHs, the concentrations and studying the effect of gamma irradiation on the remedation of PAHs through the extracted oil samples from the polluted sedments.

The high PAHs concentration levels were observed at all the sites along the outlets of the discharge basins and it may be due to the locations of the sampling points of the drainage to the outlets of the refinery, with the continuous accumulation of effluent pollutants. The difference in PAHs composition might be

related to the extent and the nature of inputs along the discharge basins.

The PAHs concentration varied significantly among the five sites from 73597.864 ng/g at the site (1), to 22333.983 ng/g at the site (5) with 43016.278 ng/g dry weights as an average concentration. It is lower at the site (5), this is consistent with the winds beside the discharge basins and the direction of the water currents.

### 3.2. PAH composition and origins in polluted sediments

The constituents of PAHs in a specified sample give consideration to the sources producing the PAH`s. From the obtained results, it was found that the PAHs with low molecular weight (LMW) 2-3 rings have a high concentration ranged from (55 – 86) %, which are (generally of petrogenic origin, belongs to petroleum, including crude oil and its refined products) related to the high abundance continues effluents from refinery to the discharge basins.

**Table (1): The PAHs concentrations in the adsorbed oil on sediment samples.**

| Site Number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Conc. PAHs (ng/g) | 73597.864 | 47384.966 | 32584.224 | 39180.36 | 22333.983 |

PAHs with high molecular weight (HMW) 4-fused rings ranged from (13,7 – 44,7) %, which are (generally of pyrogenic origin and generated by the combustion of fossil fuels and organic material) caused by the little solubility in water which decrease with the increase in the number of fused aromatic rings. This leads to increasing its ability to adsorb on the surface of sediments as a result of its hydrophobic nature. The concentrations of PAHs of HMW 5-fused rings were ranged from (0.07 – 1.8) %. Whereas the HMW of 6-fused ring their concentration ranged between (0.02 – 0.14) %. The results of the HPLC analysis facilitate us to define that the PAHs with LMW 2-3 rings are the dominant contributors and determine the proportion of pyrogenic and petrogenic origins.

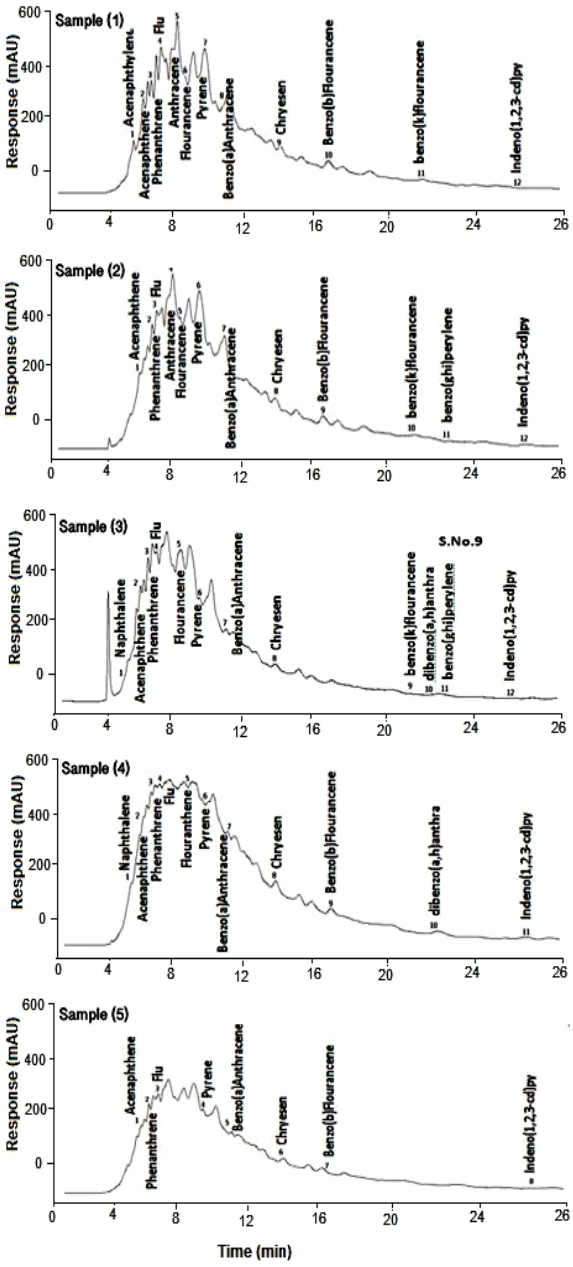


**Fig. 1. HPLC chromatograms for extracted oils from sediment samples along sites.**

### 3.3. Effect of gamma radiation on the PAHs composition

The degradation due to gamma irradiation of the PAHs attend in the extracted oil samples from the polluted sediments was studied. HPLC analysis before and after irradiation were done to evaluate the expected degradation of the PAHs.

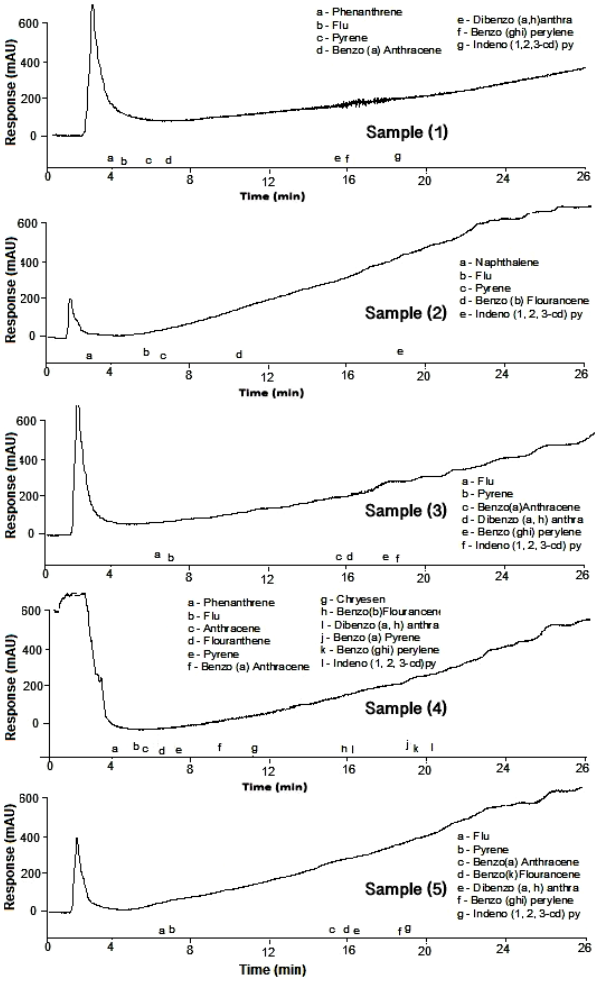


**Fig. (2): HPLC chromatograms for extracted oils from sediment samples along the outlets after irradiation with gamma rays 20 kGy**

Fig. (2) shows a forceful decrease of the concentrations of the PAHs with the gamma irradiation. The chromatograms show that gamma radiation is active in degrading all the PAHs individual composition.

The effect of gamma radiation on organic pollutants vary according to the compositions. The represented data table (2) in before and after irradiation indicates to the high effect of degradation by gamma irradiation of the oil samples. The different concentrations showed differences in the magnitude of degradation in response to the dose of gamma irradiation. The reduction in PAH concentrations was as follow: in site (1) the PAHs concentration reduced from 73597.866 ng/g to 15.0675 ng/g, in site (2) from 47384.966 ng/g to 6.5361 ng/g, in site (3) from 32584.225 ng/g to 42.6893 ng/g, in site (4) from 39180.36 to 113.686 ng/g and site (5) from 22333.983 to 177.2406 ng/g.

The gamma radiation dose of 20 kGy nearly removes all PAHs peaks with a percentage of elimination ranging from 90 to 100% as shown in (Fig. 2). The radiolytic reaction mechanism shows that the decomposition (degradation) process due to gamma rays has been often indirect, and mediated by reactive oxygen species (ROS), like single oxygen, generated by water radiolysis [22]. The PAHs ring opening due to gamma radiation suggested that the oxidation of rings. High radiation dose, doing a nearly complete transformation of simple PAHs

**Table (2):** Individual rings PAHs concentrations (ng/g dry weight) in the oil extracted from polluted sediments at the five sites before and after irradiation.

| Site No. | Ring No. | 2-Ring | 3-Ring | 4-Ring | 5-Ring | 6-Ring | Total Con. |
|---|---|---|---|---|---|---|---|
| 1 | Non – Irr. | N.D. | 61548.766 | 11558.893 | 479.0679 | 11.1407 | 73597.866 |
| | After Irr. | N.D. | 0.8778 | 2.5083 | 6.6545 | 5.0269 | 15.0675 |
| 2 | Non – Irr. | 7795.955 | 19503.977 | 20031.448 | 33.4364 | 20.1502 | 47384.966 |
| | After Irr. | N.D. | N.D | 0.58990 | 2.5187 | 3.4284 | 6.5361 |
| 3 | Non – Irr. | N.D. | 17840.436 | 14579.037 | 128.4615 | 36.2914 | 32584.225 |
| | After Irr. | N.D. | N.D. | 1.0456 | 3.4927 | 5.075 | 42.6893 |
| 4 | Non – Irr. | 15175.715 | 13004.801 | 10213.031 | 742.433 | 44.3801 | 39180.36 |
| | After Irr. | N.D. | 60.7255 | 5.7196 | 20.200 | 27.0417 | 113.686 |
| 5 | Non – Irr. | N.D. | 19214.843 | 3065.9425 | 22.7754 | 30.4232 | 22333.983 |
| | After Irr. | N.D. | N.D. | 2.8383 | 169.666 | 4.7312 | 177.2406 |

molecules of products as inorganic molecules (mineralization).

## CONCLUSION

The high residual petroleum fractions are precipitated on sediments. These residual petroleum fractions of oil cannot be completely treated or degraded easily through weathering processing, consequently, this leads to accumulation of oil residues in sediments.

To monitor the degradation of PAHs in surface sediments, the analysis by HPLC was done before and after gamma irradiation. The analyses displayed that, with the increase of the absorbed gamma dose, the radiation decreases the pollution magnitude.

The recorded results of the current work suggest that gamma irradiation for the polluted sediments improve the existing environment. So, it should be made to avoid adverse effects to public health both within the sea water and the beach.

## REFERENCES

[1] Gerges, M.A. 2002. Ocean & Coastal Management 45, 885–903.

[2] Viñas, L., Angeles, M.F., Antonio, J.S., José, J., González, J., Pon, J., Albaigés, J. 2010. Pollut. 158, 1551–1560.

[3] Abdel-Shafy, H.I., Mansour, M.S.M. 2016. Egypt. J. Pet. 25, 107–123.

[4] Marcos Almeida, Paulo DE OLIVEIRA Mafalda, Vinicius Faria Patire and Ana Cecília Rizzatti Albergaria-Barbosa. 2018. Marine Pollution Bulletin 137, 399–407.

[5] Ekpo, B.O., Fubara, E.P., Ekpa, O.D., Marynowski, H.L. 2012. Nigeria ARPN. J. Earth Sci. 1, 09–20.

[6] Le Bihanic, F., Morin, B., Cousin, X., Le Menach, K., Budzinski, H., Cachot, J. 2014. Environ. Sci. Pol. 21, 13720–13731.

[7] Oros, D.R., Ross, J.R.M. 2004. Mar. Chem. 86, 169–184.

[8] Liu, Y., Chen, L., Huang, Q.-H., Li, W.-Y., Tang, Y.-J., Zhao, J.-F. 2009a. Sci. Total Environ. 407, 2931–2938.

[9] Wagener, A., Hamacher, C., Farias, C., Godoy, J.M., Scofield, A. 2010. Mar. Chem. 121, 67–79.

[10] Dauner, A.L.L., Lourenço, R.A., Martins, C.C., 2016. Environ. Technol. Innov. 5, 41–51.

[11] Masood, N., Zakaria, M.P., Halimoon, N., Aris, A.Z., Magam, S.M., Kannan, N., Mustafa, S., Ali, M.M., Keshavarzifard, M., 2016. Mar. Pollut. Bull. 102, 160–175.

[12] Neira, C., Cossaboon, J., Mendoza, G., Hoh, E., Levin, L.A. 2017. Mar. Pollut. Bull. 114, 466–479.

[13] Barakat, A.O., Mostafa, A., Wade, T.L., Sweet, S.T., Sayed, N.B.E. 2011. Mar. Pollut. Bull. 62, 1969–1978.

[14] Fragoso, N.M., Hodson, P.V. and Zambon, S. 2006. Environmental Monitoring and Assessment, 116(1), 481-511.

[15] Duarte, C.L.,Sampa, M.H.O., Rela, P.R., Silveira, C.G., 1998. Proceedings of symposium. Zakopane, Poland. IAEA-TECDOC-1023.pp:203-210.

[16] Magi, E., Bianco, R., Ianni, C., Di carro, M. 2002. Environmental pollution.119, 91-98.

[17] Valavanidis A., Vlachogianni, Th., Triantafillaki, S., Dassenakis, M., Androutsos, F.and Scoullos, M. 2008. Coastal and Shelf Science, 79, 733-739.

[18] Liu, Y., Chen, L., Jianfu, Z., Qinghui, H., Zhiliang, Z. and Hongwen, G. 2008. Environmental Pollution, 154, 298-305.

[19] Getoff,N., 1998. Proceedings of symposium. Zakopane, Poland. IAEA-TECDOC-1023.pp:121-131.

[20] Cataldo F., Keheyan Y. 2006. Journal of radioanalytical and nuclear chemistry, 267, 3, 679-683.

[21] Dugay A., Herrenknecht C., Czok M., Guyon F., Pages N. 2002. Journal of chromatography A,958, 1-7.

[22] El-Beltagi HS, Ahmed OK, El-Desouky W. 2011. Radiation Physics and Chemistry 80 (9), 968-976.

# تطبيق إشعاع جاما فى التعامل مع التلوث البترولى من بعض معامل التكرير في منطقة خليج السويس

**نبيلة أمين على[1] , اميمة موسى[2] , *صالح محمود عبده[3]**

1. شركة السويس لتصنيع البترول – السويس - مصر
2. معهد بحوث البترول القاهرة - مصر
3. المركز القومى لبحوث وتكنولوجيا الاشعاع - هيئة الطاقة الذرية - القاهرة

يتأثر خليج السويس بالملوثات المنصرفة في الرواسب المائية. يعتبر تركيز الهيدروكربونات الاروماتية الممتزة متعددة الحلقات (PAHs) في الرواسب المائية مؤشرًا مناسبًا لحالة الملوثات في البيئة البحرية. تم جمع عينات من الرواسب من خمسة مواقع تغطي مساحة 2.5 كم على مسافات متساوية على طول منافذ أحواض التصريف في بعض مصافي البترول القريبة من خليج السويس. تم تحديد تركيزات (PAHs) عن طريق تحاليل HPLC واظهرت النتائج ان التركيزات في الرواسب في المواقع الخمسة تتراوح بين 22333.983 ± 102 و 73597.864 ± 187 نانوجرام / جرام أوزان جافة مع 43016.278 ± 149 نانوجرام / جرام أوزان جافة كمتوسط للتركيز.

تم إجراء تشعيع جاما للعينات الملوثة ومقارنتها مع العينات الملوثة غير المشعة ، وقد لوحظت انخفاض كبير جدا في تركيزات PAHs فى العينات المشعة. مما يؤكد امكانية معالجة الملوثات السامة لـ PAHs (كالمخلفات البترولية) بواسطة أشعة جاما. لذلك تمت دراسة تأثير اشعة جاما المطبقة على تدهور تركيزات مكونات PAHs في عينات الرواسب. تشير النتائج إلى أن تركيز PAHs في العينات المشعة من الرواسب تراوحت بين 16.231 ± 3.7 و 188.531 ± 12.2 نانوجرام / جرام أوزان جافة مع 82.184 ± 7.3 نانوجرام / جرام أوزان جافة كمتوسط تركيز. كما تم دراسة التباين في تركيزات PAHs في الزيوت المستخرجة مع تشعيع جاما متبوعة بتحليلات HPLC. مما يعني أن إشعاع جاما له تأثير كبير على ملوثات الهيدروكربونات الاروماتية متعددة الحلقات PAHs