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Radiological Safety Concerns in the Textile Dye Industry

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Abstract

People are frequently exposed to various harmful and allergic compounds derived from textiles. One major source of persistent organic pollutants in the environment is dye wastewater from this sector. The purpose of this study was to use gamma spectrometry with a Hyper Pure Germanium detector to determine the values of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K in different types of textile dyes (disperse, direct and reactive) and dye wastewater from different cities (Obour and Bader). The average specific activities for ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K were higher in disperse dyes than that in direct and reactive dyes. The associated potential radiation hazards were assessed. The absorbed dose rate (in $nGyh^{-1}$) was calculated for all the samples under study, with values ranging from 14 to 49 $nGyh^{-1}$ in disperse dyes, 7.6 to 21 $nGyh^{-1}$ in reactive dyes, and 7.2 to 8.8 $nGyh^{-1}$ in direct dyes. The analysis's results showed that there might be some detectable radioactivity in the textile dyes, which is something that needs to be considered. Therefore, people who work in the textile sector and those who use these dyes should follow safety guidelines and take preventative measures.

***Keywords**:* Gamma spectrometry; Radiation risks; Disperse, direct and reactive dyes; Natural radioactivity; Atomic Absorption

1. Introduction

A vast number of negative environmental effects can be attributed to the textile industry **[1]**. Particulate matter, dust, sulfur and nitrogen oxides, and volatile organic compounds are a few examples of the air pollution that is created from textile dyes. Acute toxicity to textile dyes is primarily brought on by oral intake and inhalation, particularly when dust is present and causes skin and eye irritation **[2].** Large volumes of water are contaminated by the synthetic dyes used in the textile industry. Textile colors leak into the aquatic environment as effluent because they don't cling firmly to the cloth. Therefore, ecology and public health suffer greatly when effluent from several textile enterprises is

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continuously released into the environment without being treated. Textile dyes have the potential to harm aquatic life and contaminate aquatic environments **[3]**.

They may even find their way into the food chain. Reactive, disperse and direct dyes are widely used with very different applications and dyeing processes. Water-soluble dyes known as reactive dyes are used to color synthetic and natural textiles including nylon, cotton, wool, and silk. These dyes' molecules include active groups like hydroxyl, amine, halogen, etc. that can create covalent bonds with the surface of the fiber to securely mix the dyes on the fiber. While Water-insoluble dyes called disperse dyes can be used to color synthetic fibers like acrylic, polyester, and acetate.

These dyes' molecules have both hydrophilic and hydrophobic groups, which enable them to attach to the hydrophilic areas of the fiber surface and adsorb the dyes there. To evenly scatter the dye molecules in the dyeing solution and generate tiny, dispersed particles in the liquid phase, the dyeing process of dispersing colors must be conducted under high temperature and high-pressure conditions. Disperse dyes are heat- and light-fast because the dye molecules react with hydrophilic areas on the fiber surface to produce the desired color. Direct dyes can be applied directly to the fibers and are soluble in water. They are frequently used to color cellulose textiles like rayon, cotton, and others. To increase the affinity of direct dyes for the fibers, additional chemicals or salts must be applied.

Many textile processes, such as dyeing and printing, frequently involve the usage of heavy metals **[4]**. When harmful substances are found in textile materials in higher concentrations than is advised, there may be a risk to human health from skin absorption **[5]**. Few studies determined the Concentrations of natural radioactivity and radiation hazard indices in some dyes of textiles **[5 ,6]**. This study aims to use gamma spectrometry with a Hyper Pure Germanium detector to determine the values of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K in some types of textile dyes and dyes wastewater respectively.

2. Experimental

2.1. Sample preparation

2.1.1. Textile dyes

dyes are derived from plants, animals, or minerals. Since natural dyes are sourced from organic or inorganic natural materials, radionuclides present in the environment where these sources grow or are mined can become part of the dye. For example, certain clays or minerals used for pigments may contain naturally occurring radionuclides like uranium, thorium, or potassium-40. In the present work Eighteen samples of textile dyes (6 samples

from disperse, 8 from reactive and 4 from direct) dyes with different colors were investigated. They were gathered from local suppliers who imported them from Korea and China, and they are widely used in the textile industry in Egypt.

To prepare the samples for gamma-ray studies, they were dried at 110 degrees Celsius in an oven. The 200 ml, cylindrical plastic boxes with an inner diameter equal to the detector's diameter in face-to-face geometry were used to weigh and hermetically seal the samples. Samples were carefully packed and kept for four weeks to achieve secular equilibrium between ^{226}Ra and ^{232}Th with their progenies to minimize the possibility of radon escape **[6]**.

2.1.2. Dyes wastewater

Eight samples of dyes wastewater collected from different dye factories (four samples from Obour city coded W1, W2, W3, and W4 and four samples from Bader city coded W5, W6, W7, and W8) **(Fig. 1)** were collected in identical polyethylene beakers (250 cm^3) which were also used for measurements. Each beaker was filled to the brim and a sealed cap was placed on the top to confirm that it was completely empty of air. Samples were stored for more than month to allow daughters products to reach radioactive equilibrium with the parents.

This step was necessary to ensure the radon gas is confined within the volume and the daughters remain in the sample. After the storage duration, the activity concentration of radionuclides of the studied samples are measured by using a hyper pure Germanium detector, model No. GEM-15190 in the laboratory of physics department, Faculty of women, Ain Shams University. Analysis of samples was performed, and each sample spent 140000s, approximately two days.

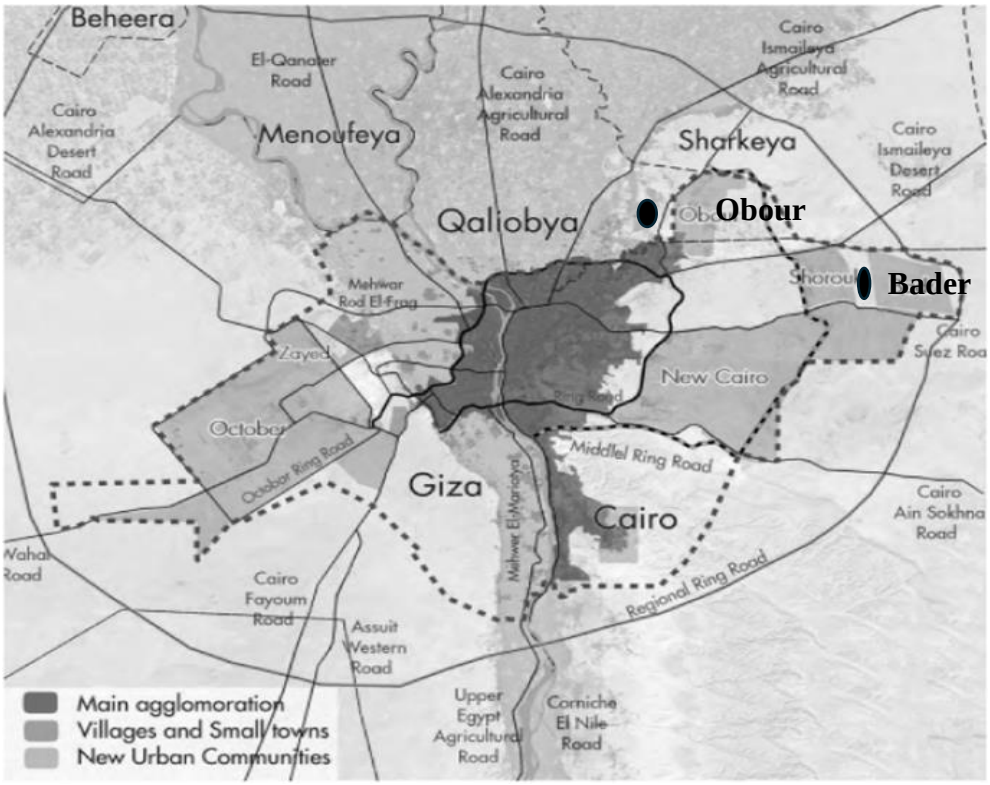

Fig. 1. Map of Obour and Bader city

2.2. Activity measurements

A high-resolution gamma detection system was used for radiometric analysis. An ORTEC model high purity germanium detector (HPGe) is used in this coaxial type of detector system with model No. GEM-1519 and serial No. 27-p-1876A. The recommended operating bias voltage is negative 3 KV. A crystal with length 47.1mm and diameter 49.3mm has been used in this detector. The HPGe detector has a full width at half maximum (FWHM) of 0.9 keV at the 122 keV gamma transition of ^{57} Co and 1.9 keV at the 1332.5 KeV of ^{60}Co gamma transition. The gamma-ray spectra data was done by using MAESTRO-32 software, and to accumulate andanalyze the data. To find the energies of any undetected gamma rays, energy calibration was used. KeV/Ch mode was used to calibrate the system. The gamma-ray energies emitted due to ^{60}Co (1173.2 and 1332.5keV) and ^{I37}Cs (661.9 keV) sources were used for the calibration **[7]**.

A ^{226}Ra point source was utilized for the HPGe detector's efficiency calibration. The relative efficiency curve for the 250 ml beakers was normalized using the concentration of chemically pure potassium chloride solution in distilled water. The absolute efficiency curve was obtained using the same sample size. The activity concentrations ^{238}U were calculated by measuring the 295.1(19.2%) and 352 (37.2%) keV γ- rays from ^{214}Pb and the 609.3 (46.1%) and 1120.3 (15.1%) keV γ -rays from^{214}Bi. ^{232}Th activity was determined from the γ -peaks of

238.6 (43.6%) keV from ^{212}Pb and 911.2 (29.0%) and 969.0 (23.2%) keV from ^{228}Ac and 583.0 (31.0%) keV γ -rays from ^{208}Tl. ^{40}K concentration was measured from its 1460 (10.7%) keV γ -line. ^{226}Ra concentration was determined by measuring the γ peak of 186 (3.3%).

3. Results

3.1. Analysis of Gamma spectrometry

The spectrum of black dye (disperse) sample is demonstrated in **(Fig. 2)** By measuring the 295.1 (19.2%), 352 (37.2%), and 1120.3 (15.1%) keV γ-rays from ^{214}Bi, and the 609.3 (46.1%) and 1120.3 (15.1%) keV γ-rays from ^{214}Pb, ^{238}U concentrations were determined. The γ-peaks of 238.6 (43.6%) keV from ^{212}Pb, 911.2 (29.0%) and 969.0 (23.2%) keV from ^{228}Ac, and 583.0 (31.0%) keV γ-rays from ^{208}Tl were used to calculate the ^{232}Th activity. ^{40}K concentration was determined from its γ-line at 1460 keV (10.7%). The γ peak of 186 (3.3%) was measured to determine the concentration of ^{226}Ra **[8]**. ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K recorded their highest average values in disperse dyes 19.14±5.17, 27.15±6.23, 8.03±2.26 and 276±37Bqkg^{-1} respectively **(Fig. 3)**. While ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K recorded their lowest average values in direct dyes 8.82±4.05, 14.48±2.77, 3.23±1.13 and 80.06 Bqkg^{-1} respectively **(Fig. 4)**.

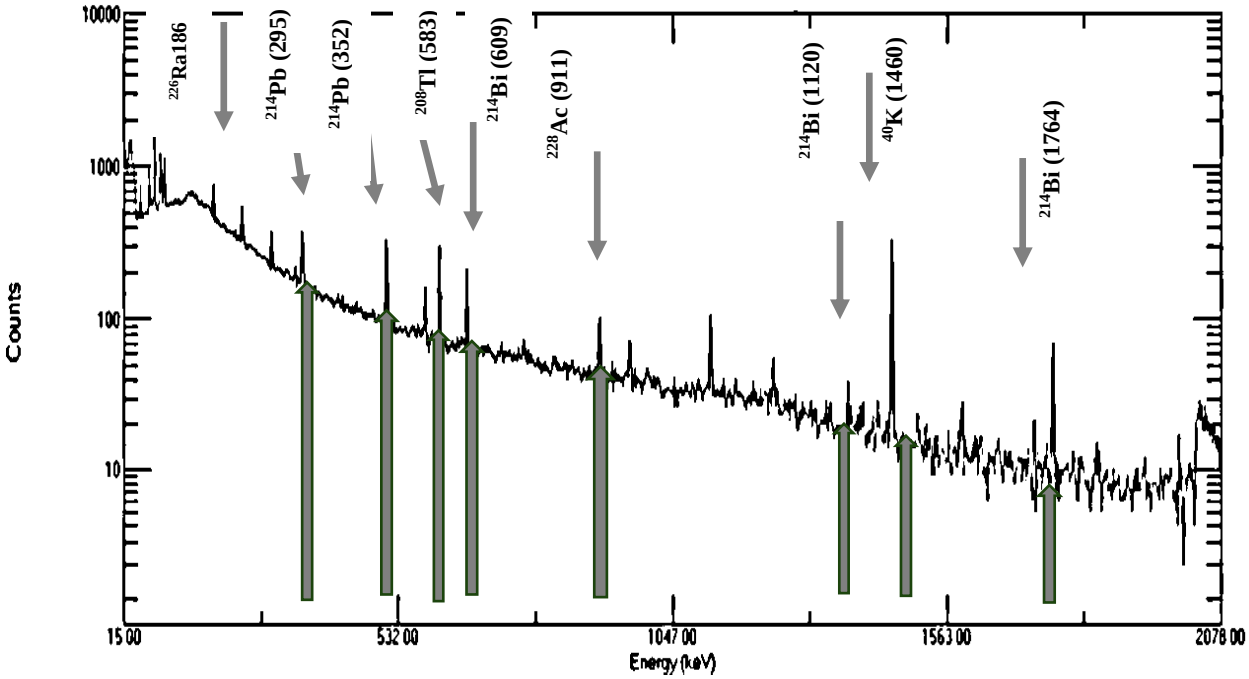

Fig. 2. Gamma- ray spectrum of the investigated black dye

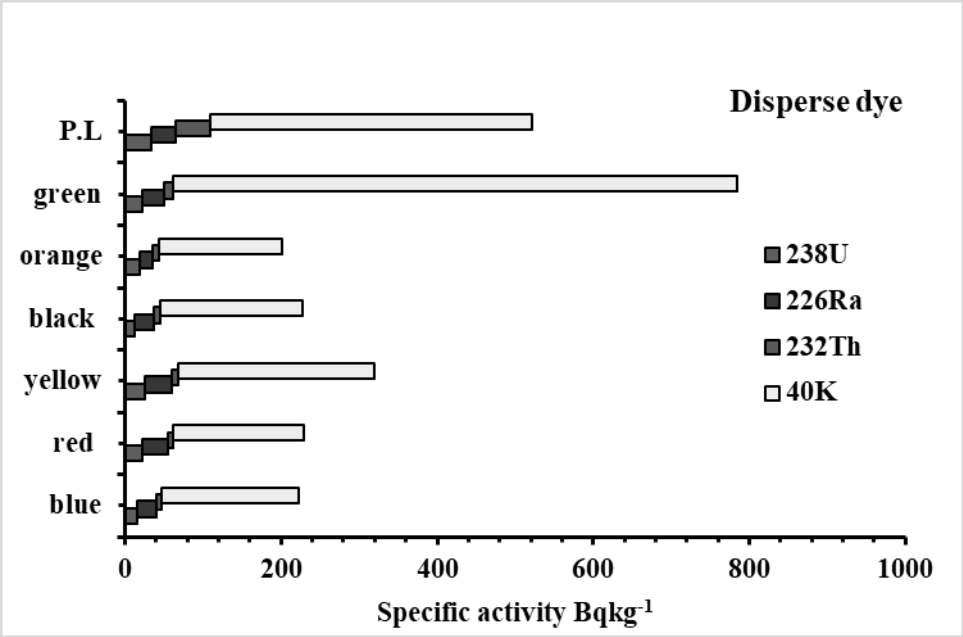

Fig. 3. Specific activity of ^{238}U, ^{226}Ra, ^{232}Th and ^{40} K in disperse dye samples.

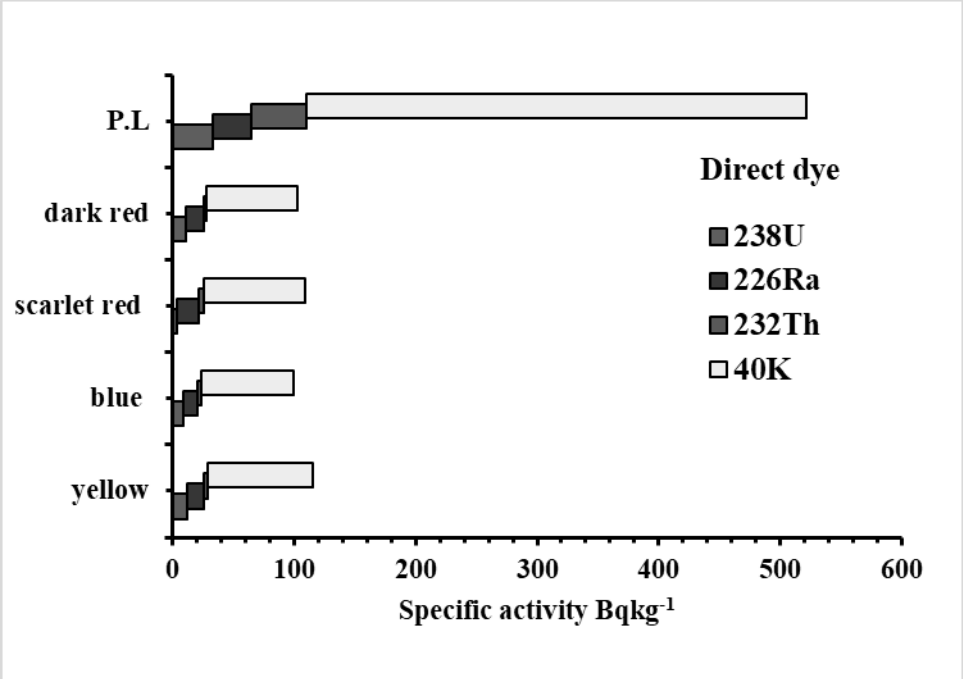

Fig. 4 Specific activity of ^{238}U, ^{226}Ra, ^{232}Th and ^{40} K in direct dye samples.

In reactive dyes the values of ^{238}U ranged from 3.95 to 22.61 Bqkg^{-1} with an average value of 13.97±3.7 Bqkg^{-1}. While the mean ^{226}Ra specific activity was 17.81±9.2 Bqkg^{-1}. The highest value of ^{226}Ra (31.23± 7.16 Bqkg^{-1}) was recorded in yellow dye while the lowest value (3.8±0.70 Bqkg^{-1}) was observed in black dye. ^{232}Th recorded lowest value (0.935±0.2 Bqkg^{-1}) in red dye where the highest value recorded in brown dye (7.35± 2.0 Bqkg^{-1}). The mean specific activity of ^{40}K was 153±20 Bqkg^{-1} and recorded its highest value (279±37 Bqkg^{-1}) in red dye and recorded its lowest value (87±11Bqkg^{-1}) in green dye **(Fig. 5)**. For the

first time we determine the natural radioactivity in dyes wastewater. In the present work there are some factories of dyes wastewater in Obour and Bader cities**.** ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K recorded their highest average values in Obour 11.28±1.2, 17.87±3.3, 3.41± 0.9 and 127±3.5 Bqkg^{-1} respectively **(Fig. 6)**.

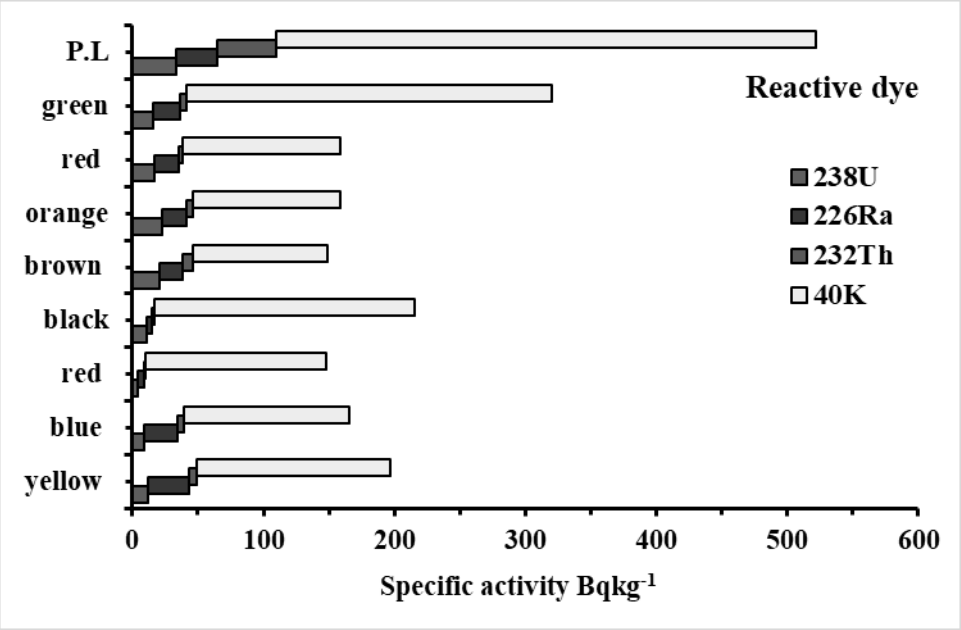

Fig. 5 Specific activity of ^{238}U, ^{226}Ra, ^{232}Th and ^{40} K in reactive dye samples.

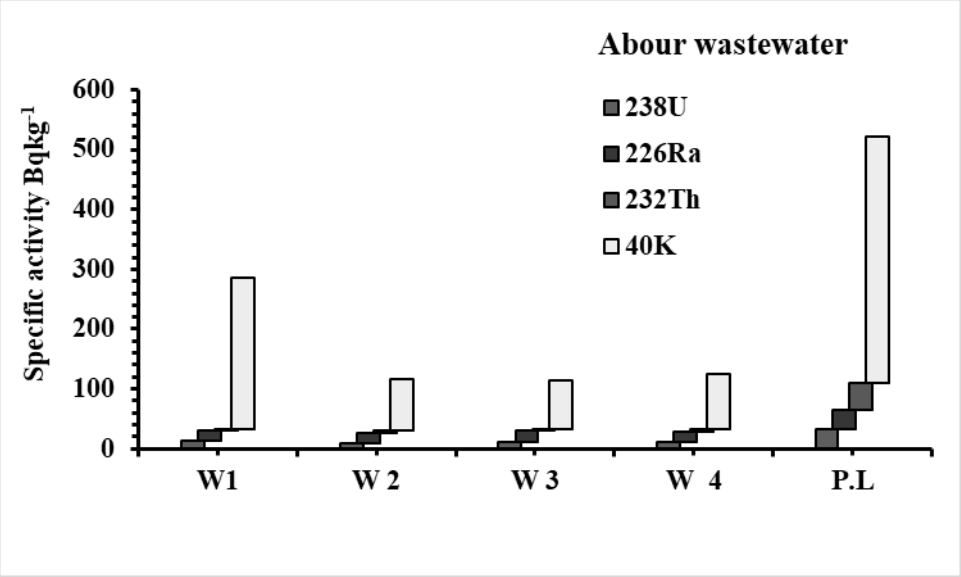

Fig. 6 Specific activity of ^{238}U, ^{226}Ra, ^{232}Th and ^{40} K in Obour wastewater samples.

While in Bade ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K recorded 9.96±1.9, 13.34±1.2, 3.70±0.9 and 89±5.9 Bqkg^{-1} respectively **(Fig. 7)**.

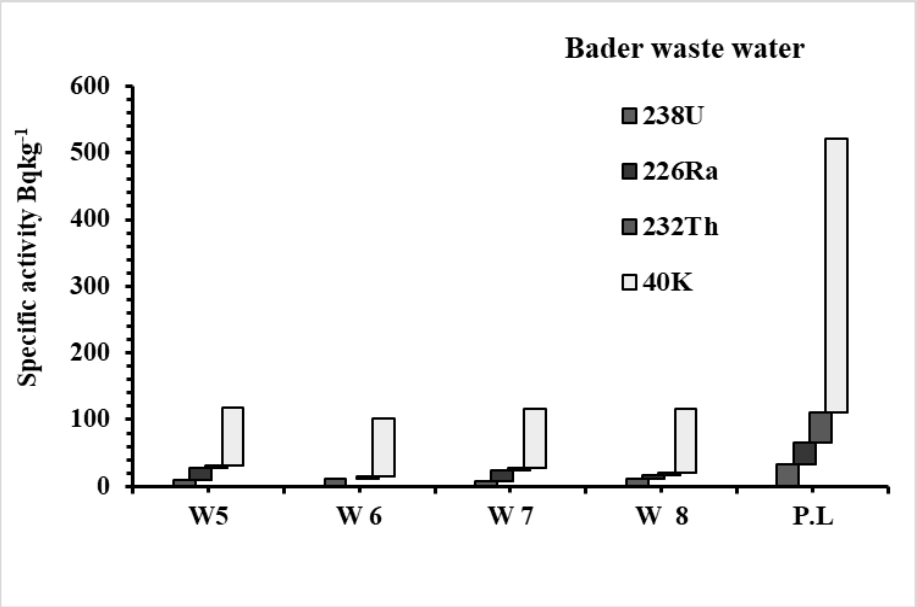

Fig. 7 Specific activity of ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K in Bader wastewater samples.

3.2. Radiological hazards

Different hazard indices were calculated in the investigated samples such as radium equivalent activity (Ra_{eq}), internal and external hazard indices (Hin, Hex), and outdoor and indoor excess lifetime cancer risk (ELCRout, ELCRin) **(Table 1)**.

The results demonstrated that the lowest value of radium equivalent (Ra_{eq}) was 6.7± 0.13 $Bqkg^{-1}$ in direct dye (yellow sample), while the highest value 100 ± 2.2 $Bqkg^{-1}$ was recorded in disperse dyes (green sample) **(Table 2)**. So, all investigated samples were less than the maximum permissible value of 370 $Bqkg^{-1}$ **[18].** The gamma index (I_γ) for the investigated samples is demonstrated in **(Table 2)**, where the index values ranged from 0.10 to 0.78, in disperse dyes, 0.08 to 0.36 in reactive dyes, and from 0.06 to 0.22 in direct dyes. All values lie within the acceptable range.

The external and internal hazard indices (H_{ex}, H_{in}) due to the emitted gamma-rays for investigated samples were calculated and found to be less than unity. Also the total absorbed dose rate **D** (in $nGyh^{-1}$) due to exposure to gamma radiation (emitted by ^{214}Pb and ^{214}Bi progeny of ^{238}U and ^{228}Ac and ^{208}Tl progeny of ^{232}Th as well as the ^{40}K contributions) was calculated in all samples under study and it ranged from 14 to 49 in $nGyh^{-1}$ in disperse dyes, from 7.6 to 21 $nGyh^{-1}$ in reactive dyes and from 7.2 to 8.8 in direct dyes **(Table 2)**. This value was lower than the international recommended value (55 $nGyh^{-1}$) **[18].**

The annual equivalent dose rates in all samples investigated were still lower than the recommended limit of 1.5 $mSvyear^{-1}$ as suggested by **NEA-OECD [19].** In addition to hazard

indices, outdoor excess lifetime cancer risk due to radiation exposure (ELCRout) was calculated.

The highest average values of outdoor excess lifetime cancer risk were observed in disperse dyes (0.19 ± 0.006). These values are lower than the world's average 0.29 **[20].** Also, **Table 3** demonstrates radiation hazard indices in dyes wastewater in Obour and Bader factories where the average of all hazard indices such as Ra_{eq}, I_{γ}, H_{ex}, H_{in}, D_{out}, E_{out}, and ELCR recorded highest values (18 $Bqkg^{-1}$, 0.14, 0.045, 0.10, 12.10, 0.012, and 0.047 respectively) in Obour factory than that in Bader factory (12 $Bqkg^{-1}$, 0.07, 0.03, 0.09, 10.60, 0.01, and 0.04 respectively)

4. Discussion

Variations in radionuclide concentrations among different dye colors, types, and wastewater sources can be influenced by several factors, such as sources of raw materials, geological formations, chemical composition of dyes and manufacturing processes. **[21-24]**. Previously, we determined the values of ^{238}U, ^{232}Th, and ^{40}K, in nine different dyes employed in the textile industry using gamma spectrometry with a Hyper Pure Germanium (HPGe) detector and we found that the mean activity concentrations of ^{238}U, ^{232}Th and ^{40}K were 29.37 ± 4.48, 1.15 ± 0.13 and 565 ± 4 $Bqkg^{-1}$, respectively **[6]**. Also, we determine the values of both radon and thoron (6978 ± 2491 and 3457 ± 996 Bqm^{-3}, respectively) **[4]**. The mean activity concentrations (^{238}U, ^{232}Th, and ^{40}K) in previous work are higher than that in the present work (19.14± 5.1 ,8.08±2.2 and 276 ± 37 respectively in disperse dyes, 8.82± 2.0, 3.23±0.1 and 80.06 ±10 in direct dyes and 13.97± 3.7, 3.96±0.1 and 153.36± 20 respectively in reactive dyes.

These results indicated that the textile dyes may possess a measurable amount of radioactivity that should be considered. So, in the present work we analyze different categories of textile dyes such as reactive, disperse and direct dyes. Radiation hazard indices in all categories of investigated textile dyes are at the recommended levels. Also, all radiation hazard indices were calculated in dyes wastewater in Obour and Bader cities. The results demonstrated that (i) all radiation hazard indices in Obour city are greater than Bader city. (ii) all recorded values are lower than the permissible levels **(Table 3).**

Table 1 Radiation hazard indices in the investigated samples

Hazard indices	Definition	Formula
Radium equivalent Ra_{eq} ($Bqkg^{-1}$)	Radium equivalent activity (in $Bqkg^{-1}$) has been used to quantify radiation exposure to compare the specific activity of materials containing varying concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in a single value **[9,10]**.	$Raeq = C_{Ra} + 1.43C_{th} + 0.077C_k$
Gamma index Iγ	Because of the excess external gamma radiation from surface material, the index Iγ has a correlation with the annual dosage rate **[11]**.	$I_\gamma = \frac{C_{Ra}}{300} + \frac{C_{Th}}{200} + \frac{C_K}{3000}$
External and internal hazard indices (H_{ex} and Hin)	Both the interior and exterior hazard indices (Hex and Hin) are used for predicting the effects of radiation on human health.	$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/4810$ $H_{in} = C_{Ra}/185 + C_{Th}/259 + C_K/4810$
Absorbed dose rate Dair (nGy h 1)	dose rate exposure to radiation sources in the air at one meter due to the concentrations (A) of ^{238}U, ^{232}Th, and ^{40}K **[12,13].**	$D = [0.662\ C_{Th} + 0.427\ C_U + 0.0432\ C_K]$
Outdoor annual effective dose AEDin (mSv y 1)	measure radiation exposure both indoors and outdoors during a one-year period **[14,15].**	**Effective dose rate (mSv/ year) = Dose rate ($nGy\ h^{-1}$) 8760 h x 0.2 x 0.7 Sv Gy^{-1} x10^{-6}**
Excess Lifetime Cancer Risk – (ELCR)	chance of developing cancer in the long run for specific levels of exposure **[16,17]**.	$ELCR_{out} = E_{out} \times 66 \times 0.05$

Table 2 Radiation hazards indices in different textile dyes

Dye category	Samples	Ra_{eq}	Iγ	H_{ex}	H_{in}	D(out)	E(out)	ELCR (out)
Disperse	blue	48	0.35	0.13	0.15	18	0.02	0.07
	red	54	0.38	0.14	0.19	20	0.02	0.08
	yellow	65	0.47	0.17	0.24	27	0.03	0.011
	black	50	0.36	0.13	0.14	17	0.02	0.07
	orange	12	0.10	0.03	0.15	14	0.01	0.05
	green	100	0.78	0.27	0.33	49	0.05	0.19
Reactive	yellow	50	0.36	0.13	0.12	15	0.02	0.06
	blue	42	0.30	0.11	0.10	12	0.01	0.05
	red	11	0.09	0.02	0.05	7.6	0.01	0.03
	black	15	0.13	0.04	0.11	13	0.02	0.05
	brown	7.9	0.06	0.02	0.15	13	0.01	0.05
	orange	34	0.24	0.09	0.18	17	0.02	0.07
	deep red	9.2	0.08	0.02	0.13	12	0.01	0.04
	green	28	0.23	0.07	0.18	21	0.02	0.08
Direct	yellow	6.7	0.06	0.02	0.09	8.8	0.01	0.03
	blue	17	0.13	0.05	0.07	7.2	0.01	0.03
	red	31	0.22	0.08	0.05	8.0	0.01	0.03
	Dark red	20	0.14	0.05	0.08	7.9	0.01	0.03

Table 3 Radiation hazards indices in dyes wastewater

Wastewater source	Samples	Ra_{eq}	Iγ	H_{ex}	H_{in}	D(out)	E(out)	ELCR (out)
Obour	W1	36	0.28	0.09	0.14	16.83	0.02	0.07
	W2	11	0.09	0.03	0.08	9.80	0.01	0.04
	W3	12	0.09	0.03	0.10	10.9	0.01	0.04
	W4	13	0.10	0.03	0.09	10.9	0.01	0.04
Bader	W5	11	0.09	0.03	0.09	10.03	0.01	0.04
	W6	12	0.09	0.03	0.10	10.68	0.01	0.04
	W7	12	0.01	0.03	0.08	10.05	0.01	0.04
	W8	13	0.10	0.04	0.10	11.38	0.01	0.04

5. Conclusions

The present study determines the natural radioactivity (^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K) and its radiological hazards in three different categories of textile dyes (disperse, direct and reactive). The result confirms that the values of specific radioactivity are higher in disperse dyes than others. Disposal of dye-containing waste can lead to soil pollution, affecting plant life and potentially entering the food chain. So, more studies should be done on stained textile dyes industry.

6. Declarations

1. **Conflicts of interest:** The authors declare that there are no conflicts of interest.
2. **Funding:** This research received no external funding.
3. **Data availability:** Data sharing is not applicable to this article where the manuscript includes all the data we generated.

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الملخص العربي

المخاوف المتعلقة بالسلامة الإشعاعية في صناعة صبغ المنسوجات

سامح فودة - ايمان عبد الحليم - هيام عبد الغنى

قسم الفيزياء كلية البنات للأدب والعلوم والتربية – جامعة عين شمس – القاهرة- مصر

الملخص العربى:

يتعرض الناس بشكل متكرر لمختلف المركبات الضارة والمسببة للحساسية المستمدة من المنسوجات .أحد المصادر الرئيسية للملوثات العضوية الثابتة في البيئة هو مياه الصرف الصحي للصبغة من هذا القطاع .كان الغرض من هذه الدراسة هو استخدام مطياف جاما مع كاشف الجرمانيوم عالي النقاء لتحديد قيم اليورانيوم- ٢٣٨ والراديوم- ٢٢٦ والثوريوم- ٢٣٢ والبوتاسيوم- ٤٠ في أنواع مختلفة من أصباغ النسيج (المشتتة والمباشرة والتفاعلية) ومياه الصرف الصحي للصبغة من مدن مختلفة (عبور وبدر) .كان متوسط الأنشطة النوعية لكل من اليورانيوم- ٢٣٨ والراديوم- ٢٢٦ والثوريوم- ٢٣٢ والبوتاسيوم- ٤٠ أعلى في الأصباغ المشتتة من تلك الموجودة في الأصباغ المباشرة والتفاعلية .تم تقييم أخطار الإشعاع المحتملة المرتبطة .أظهرت نتائج التحليل أنه قد يكون هناك بعض النشاط الإشعاعي القابل للكشف في أصباغ النسيج، وهو أمر يجب مراعاته .لذلك، يجب على الأشخاص الذين يعملون في قطاع النسيج وأولئك الذين يستخدمون هذه الأصباغ اتباع إرشادات السلامة واتخاذ التدابير الوقائية.