The Ability of Raman Spectroscopy to Detect Surface Water Pollution in Northern Sudan

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ABSTRACT

Water pollution is a complex problem for people in Sudan, especially in the northern state. Human activities such as Gold exploration, use of fertilizers in agriculture and industrial activities are, more or less directly, responsible for increasing pollution in running waters. This study aims to detecting the contaminants present in surface water in Northern Sudan.

Five samples of water lines from different drinking water treatment plant were collected. the samples were analyzed by Horiba Lab RAM 3D Raman spectrometer. The results showed that the samples beside the water contain toxic and dangerous substances that may lead to dangerous diseases, in different quantities, such as: cyanide, nitrate, Uranium oxide and phenol.

KEYWORDS: Raman spectroscopy; Surface water pollution; dangerous diseases; water treatment plant; Northern Sudan

1. INTRODUCTION

Clean water is so basic to human life that water droplets, bubbling brooks, and waterfalls are enduring symbols of the life force. Obtaining an adequate supply of clean water has likely always been a challenge for much of humanity [1]. Despite the scientific and technological advancements of the modern society and, ironically, sometimes because of them, clean water is becoming an increasingly scarce and coveted resource. From these considerations, one has that water security is now a critical environmental issue that touches the life of every human being [2].

The increasing world population with growing industrial demands has led to a situation where protection of the environment has become a major issue and a crucial factor for several industrial processes, which will have to meet the requirements of the sustainable development.

Theoretical Basis of Raman Spectroscopy

Raman Spectroscopy effect was discovered by Indian physicists C.V. Raman in 1928 but only instrumental developments from 1980s brought about big progress of Raman techniques. Although Raman Spectroscopy process is intrinsically weak, Raman spectroscopy has become nowadays a routine method in many fields.[3]

Raman scattering is relies on inelastic scattering of monochromatic light, (usually from a laser in the visible, near infrared, or near ultraviolet range) by matter.

As in figure 1 the molecular system has two vibrational energy levels, the ground state and the excited state which are separated by the energy $h\nu_M$, where ν_M is the frequency of the molecular vibration. The incident light with energy $h\nu_L$ induces transitions to virtual levels. Returning to the initial state takes place in three different ways, namely by emitting light of frequencies ν_L, $\nu_L - \nu_M$, and $\nu_L + \nu_M$. Rayleigh scattering arises from a transition that starts and finishes at the same vibrational energy level. The shifts to lower frequency called Stokes and higher frequency called as anti-Stokes Raman scattering. Stokes Raman scattering arises from a transition that starts at the ground state

vibrational energy level and finishes at a higher vibrational energy level, whereas anti-Stokes Raman scattering involves a transition from a higher to a lower vibrational energy level. The anti-Stokes transitions are less likely to occur than the Stokes transitions, resulting in the Stokes Raman scattering being more intense. The intensity of Raman scattering is proportional to the square of the change in the molecular polarizability α resulting from a normal mode q: [4].

$$I_{RA} \propto \left(\frac{\partial \alpha}{\partial q}\right)$$

Otherwise stated, a vibrational mode that satisfies the requirement

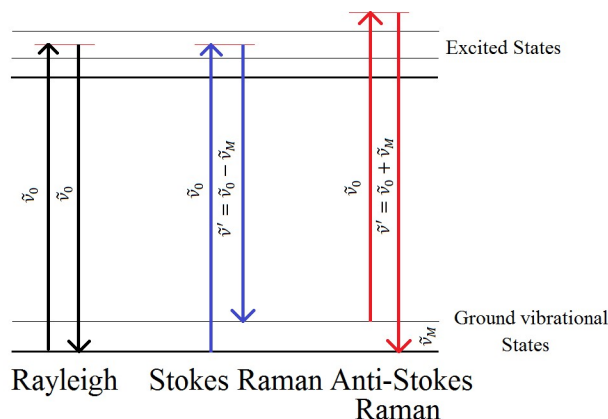$$\left(\frac{\partial \alpha}{\partial q}\right) \neq 0$$

Figure 1: The diagram the energy diagram of a molecule showing the Raman scattering.

Over the last decade, Raman spectroscopy has gained more and more interest in research as well as in identification and characterization of materials. As a vibrational spectroscopy technique, it is complementary to the also well-established infrared spectroscopy. Through specific spectral patterns, substances can be identified and molecular changes can be observed with high specificity.[5]

2. Materials and Methods
I. Materials
Five samples of Surface water were collected from water treatment plant from different regions in northern Sudan (Abohamd, Abry, Atbra, Halfa, and Shandy). Each sample was put in the glass substrate of the spectrometer and Raman spectrum was recorded in the region from 300 to 2800 cm^{-1}. The Raman shift in wavenumber, and the change in intensities of the scattered light in Raman spectra were compared with data in the previous studies and references. The map below shows the areas which samples were taken from.

The map of areas which samples were taken from

II. Instrumentation
Laser Raman microscope spectrometer model Horiba Lab RAM HR D3, shown in the Figure 2 was used. The light source of this spectrometer is Nd-YAG laser with wavelength of 532 nm and output power of 6mW.

Figure2: Laser Raman spectrometer model Horiba Lab RAM 3D

3. Results and discussion
Figure 3 shows the Raman spectrum of a sample which taken from the water treatment plant in the area of Abohamd in the range from 456 to 2630 cm^{-1}.Clear peaks were observed and by comparison with the vibrations recorded in previous studies and some references, we found that these vibrations describe the vibrations of water molecules and some components of other materials as listed in Table 1.
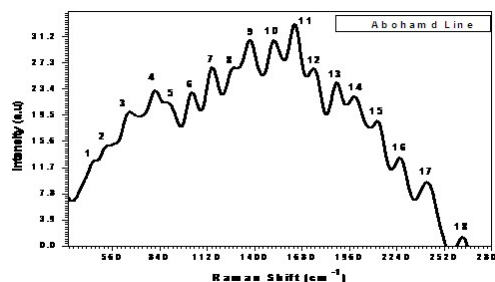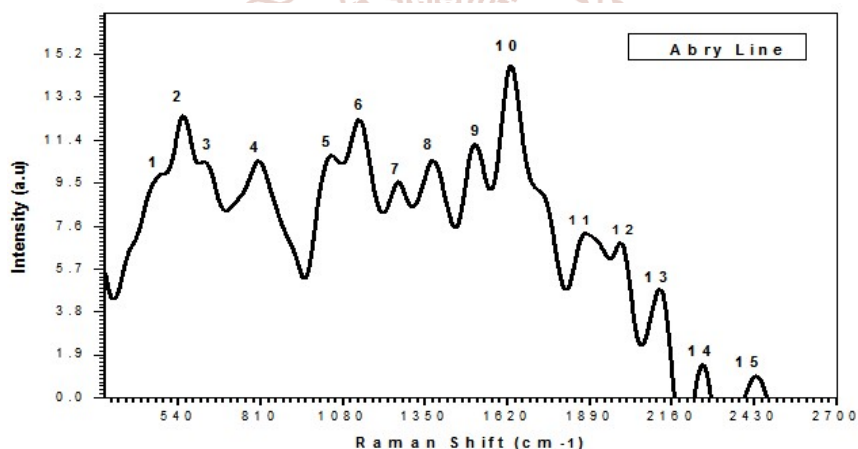

Figure 3: Raman spectrum of water sample taken from Abohamd in the range from 456 to 2630 cm^{-1}.

Table1: water sample collected from Abohamd water treatment plant

Peak number	Peak Wavenumber CM^{-1}	Intensity a.u	Functional group	References
1	456	12.85	Si-O-Si	[6,7,8,9]
2	538	15.07	Si-O-Si	[7, 8,9,14]
3	660	20.12	FeIII-O	[10]
4	810	23.37	v(C-C) stretching vibration	[11]
5	891.7	21.50	UO_2^{+2} antisymmetric Stretching	[24]
6	1030	23.03	δ (C–H) δ: bending mode	[12]
7	1152	26.80	Toluene	[13]
8	1270	26.72	V(C-B) β	[19]
9	1374.1	30.91	Ethylbenzene	[13]
10	1510.9	30.83	C = C	[7,9,14,15]
11	1635	33.22	O-H bending	[16]
12	1752	26.55	Lactone	[7,14]
13	1876	24.48	C=O stretching	[20]
14	1990	22.43	-	-
15	2121.3	18.76	Isothiocyanate	[7,14]
16	2262	13.27	Diazonium salt	[7,14]
17	2411.6	9.60	P – H	[7,14]
18	2630	1.47	-	-

The Raman spectrum of a sample which taken from the water treatment plant in the area of Abry in the range from 481 to 2436 cm^{-1} as shown in figure 4 beside the vibrations of water molecules some other vibrations were appeared in the spectrum. As shown in Table 2.

Figure 4: Raman spectrum of water sample taken from Abry in the range from 481 to 2436 cm^{-1}.

Table2: water sample collected from Abry water treatment plant

Peak number	Peak Wavenumber CM^{-1}	Intensity a.u	Functional group	References
1	481	9.94	-	-
2	545	12.56	Si -O- Si	[8,9]
3	625.1	10.48	C = S	[7,14]
4	810	10.56	v(C-C) stretching vibration	[11]
5	1041.3	10.81	Sulfonic acid	[7,14]
6	1136	12.39	V$_3$symmetric stretching of the per chlorate ion	[21]
7	1257	9.61	C-O	[16]
8	1374.1	10.56	Ethylbenzene	[13]
9	1510.9	11.27	C = C	[7,9,14,15]
10	1635	14.76	O-H bending	[16]
11	1877	7.32	NO	[17]
12	1988	6.91	-	-
13	2121.3	4.87	Isothiocyanate	[7,14]
14	2262	1.55	Diazonium salt	[7,14]
15	2436	1.00	-	-

Figure 5 illustrates Raman spectrum of the water collected from the water treatment plant in the area of Atbra in the range from 389 to 2403 cm^{-1}. Table 3 lists the analysis of this spectrum.
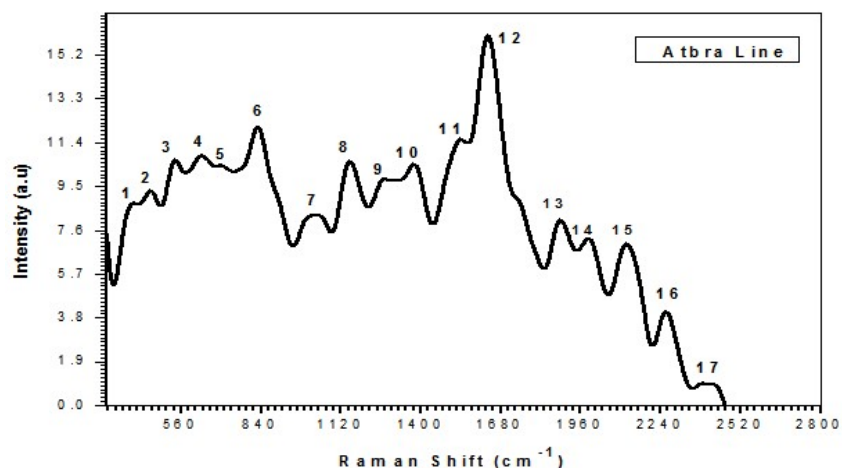
Figure 5: Raman spectrum of water sample taken from Atbra in the range from 389 to 2403 cm^{-1}.

Table 3: water sample collected from Atbra water treatment plant

Peak number	Peak Wavenumber cm-1	Intensity a.u	Functional group	References
1	389	8.86	α Fe-OH	[10,23]
2	456	9.40	Si-O-Si	[6,7,8,9]
3	538	9.60	Si-O-Si	[7, 8,9,14]
4	635	10.90	Acetylene C–H bending	[22]
5	704	10.48	CaCO3	[18]
6	840	12.19	As–O asymmetric vibration	[22]
7	1030	8.32	δ (C–H) δ: bending mode	[2]
8	1152	10.65	Toluene	[13]
9	1270	9.90	V(C-N) β	[19]
10	1377	10.53	Toluene	[13]
11	1535	11.60	amide II	[20]
12	1635	16.14	O-H bending	[16]
13	1899.4	8.11	C = C	[7,9,14,15]
14	1984	7.32	-	-
15	2121.3	7.08	Isothiocyanate	[7,14]
16	2262	4.16	Diazonium salt	[7,14]
17	2403	1.05	P – H	[7,14]

The Raman spectrum of a sample taken from collected from the water treatment plant in the area of Halfa in the range from 389 to 2432 cm^{-1} as figure 6 shows. it shows clear peaks and by comparison with the vibrations recorded in some references, we found that these vibrations describe the vibrations of water molecules and some components of other materials as listed in Table 4.
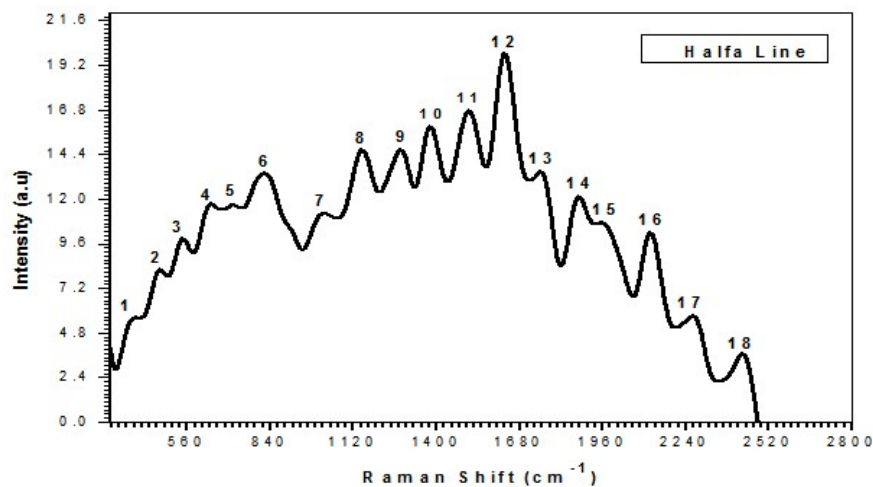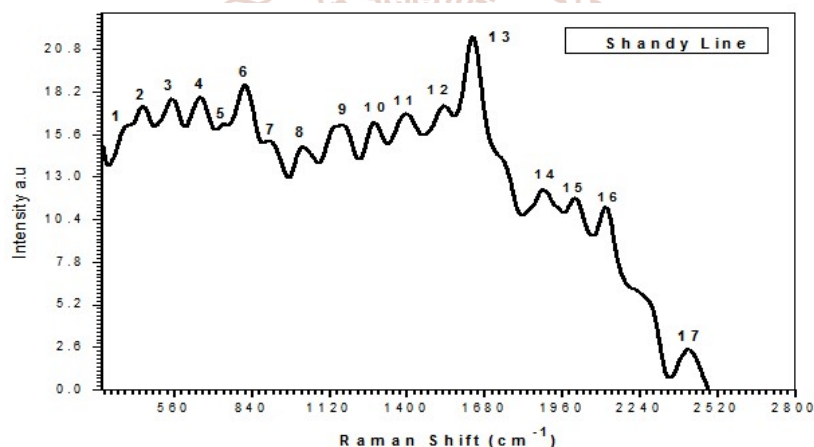

Figure 6: Raman spectrum of water sample taken from Halfa in the range from 389 to 2432 cm^{-1}.

Table4: water sample collected from Halfa water treatment plant

Peak number	Peak Wavenumber cm-1	Intensity a.u	Functional group	References
1	389	5.71	α Fe-OH	[10,23]
2	464	8.29	Si-O-Si	[7,8,9,14]
3	545	9.97	Si -O- Si	[8,9]
4	641	11.84	C=S	[7,8,14]
5	717.2	11.79	p-xylene	[13]
6	822	13.45	$(ASO_4)^{-3}$ symmetric stretching	[24]
7	1026	11.30	Toluene	[13]
8	1152	14.75	Toluene	[13]
9	1270	14.75	V(C-N) β	[19]
10	1377	16.04	Toluene	[13]
11	1510.9	16.84	C = C	[7,9,14,15]
12	1635	19.97	O-H bending	[16]
13	1752.5	13.56	Lactone	[7.14]
14	1877	12.23	NO	[17]
15	1960	10.82	-	-
16	2121.3	10.34	Isothiocyanate	[7.14]
17	2262	5.82	Diazonium salt	[7.14]
18	2432	3.77	-	-

Figure 7 illustrates Raman spectrum of the a sample which collected from the water treatment plant in the area of area of Shandy in the range from 389 to 2411.6 cm^{-1}. Table 5 lists the analysis of this spectrum.

Figure7: Raman spectrum of water sample taken from Shandy in the range from 389 to 2411.6 cm^{-1}.

Table5: water sample collected from Shandy water treatment plant

Peak number	Peak Wavenumber cm-1	Intensity a.u	Functional group	References
1	389	16.26	α Fe-OH	[10,23]
2	448	17.44	S-S	[7,8,9,14]
3	545	17.90	Si -O- Si	[8,9]
4	650	18.01	FeII-O	[25]
5	737	16.38	-	-
6	810	18.74	v(C-C) stretching vibration	[11]
7	891.7	15.31	$UO2^{+2}$ antisymmetric Stretching	[24]
8	1026	14.97	Toluene	[13]
9	1152	16.31	Toluene	[13]
10	1270	16.43	V(C-N) β	[19]
11	1396.6	16.94	Aromatic azo	[7,14]
12	1535	17.44	amide II	[20]
13	1635	21.72	O-H bending	[16]
14	1890	12.33	-	-
15	2004	11.81	-	-
16	2121.3	11.26	Isothiocyanate	[7,14]
17	2221.5	6.20	Aromatic nitrile	
18	2411.6	2.60	P – H	[7,14]

After analysis, it was found that, surface water samples contaminated by toxic substances with different concentrations such as follow:

In Abohamd region water contaminated by $(UO_2^{+2}, v(C-N)_\beta$, P – H and Ethylbenzene) with intensities (21.50, 26.72, 9.60 and 30.91) respectively.

In Abry region water contaminated by (Ethylbenzene and NO) with intensities (10.56 and 7.32) respectively.

In Atbra region water contaminated by ($v(C-N)_\beta$ and P – H) with intensities (9.90 and 1.05) respectively.

In Halfa region water contaminated by $((ASO_4)^{-3}, v(C-N)_\beta$ and NO) with intensities (13.45, 14.75 and 12.23) respectively.

In Shandy region water contaminated by (S-S, UO_2^{+2}, P – H and $v(C-N)_\beta$) with intensities (17.44, 15.31, 2.60 and 16.43) respectively.

cyanide is highly toxic. The cyanide anion is an inhibitor of the enzyme cytochrome c oxidase in the fourth complex of the electron transport chain (found in the membrane of the mitochondria of eukaryotic cells). It attaches to the iron within this protein. The binding of cyanide to this enzyme prevents transport of electrons from cytochrome c to oxygen. As a result, the electron transport chain is disrupted, meaning that the cell can no longer aerobically produce ATP for energy. Tissues that depend highly on aerobic respiration, such as the central nervous system and the heart, are particularly affected. This is an example of histotoxic hypoxia.

Nitrate poisoning can occur through enterohepatic metabolism of nitrate due to nitrite being an intermediate. Nitrites oxidize the iron atoms in hemoglobin from ferrous iron(II) to ferric iron(III), rendering it unable to carry oxygen. This process can lead to generalized lack of oxygen in organ tissue and a dangerous condition called methemoglobinemia. Although nitrite converts to ammonia, if there is more nitrite than can be converted, the animal slowly suffers from a lack of oxygen.

Arsenate can replace inorganic phosphate in the step of glycolysis that produces 1,3-bisphosphoglycerate from glyceraldehyde 3-phosphate. This yields 1-arseno-3-phosphoglycerate instead, which is unstable and quickly hydrolyzes, forming the next intermediate in the pathway, 3-phosphoglycerate. Therefore, glycolysis proceeds, but the ATP molecule that would be generated from 1,3-bisphosphoglycerate is lost – arsenate is an uncoupler of glycolysis, explaining its toxicity.

4. Conclusion
Raman spectroscopy is a powerful tool that allows to carry out an accurate quantitative analysis of concentrations of species present in the surface water. Accordingly, we recommend the Ministry of Water and Irrigation in Sudan to improve the work and efficiency of drinking water treatment plants in Northern Sudan, as well as increase the number of water treatment plants.

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