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CHARACTERIZATION OF THE SLUDGE OF IBN ZIAD CONSTANTINE SEWAGE TREATMENT PLANT FOR ITS LANDSPREADING

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Abstract: The purpose of this study was to determine the content of metals elements in the sludge of Ibn Ziad sewage treatment plant of Constantine in order to preserve its quality for subsequent use in agriculture. The use of X-ray fluorescence spectroscopy allowed us to identify the following constituents in this mud: Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Ba, Pb. These elements represent 49.82 % of the total mass of the sludge. The elements present with regulated content limit are chromium, copper, nickel, lead and zinc. They occur respectively with the following concentrations: 0.27 $mg \cdot g^{-1}$, 0.48 $mg \cdot g^{-1}$, 0.11 $mg \cdot g^{-1}$, 0.35 $mg \cdot g^{-1}$ and 2.70 $mg \cdot g^{-1}$. We have achieved an extraction for evaluating the concentration of the dissolved nitrate ions, the chemical oxygen demand (COD), and *p*H. The nitrate ions were transformed into sodium paranitrosalicylate to be dosed by ultraviolet-visible (UV-Vis) spectroscopy at 420 nm. The concentration measured was 0.12 $mg \cdot g^{-1}$. The measuring of the COD issued a value of 0.45 $mg \cdot g^{-1}$. *p*H was 7.1.

Keywords: *element trace, landspreading, sewage treatment plants, sludge*

INTRODUCTION

Algeria today has about 165 mechanical sewage treatment plants, and plans to double this amount within the coming years. This rise will have a direct impact on the quality of the environment and will increase the watered areas with treated water from the stations [1]. It will also make waste materials processing problems of these stations get worse. Our study is concerned with the characterization of the sludge in the Ibn Ziad sewage treatment plant of Constantine within the perspective of its valorization. This station has a treatment capacity of 450,000 population equivalents, sized for a mean flow equivalent to 69120 $m^3 \cdot day^{-1}$. Considering that the treatment of one population equivalent generates about 40 kg dry sludge materials per year. This station will therefore be able to produce over 18 tons of sludge per year. The mechanized stations produce dehydrated sludge that needs to be constantly cleared. This sludge is composed of complex organic matters, inorganic materials, and microorganisms.

There are three main ways for the elimination of these wastes: incineration [2], landfilling, and sludge spreading (agricultural landspreading). During incineration, the sludge is burned and the smokes produced are treated and then the ashes are cleared [3]. This involves a high treatment cost. Landfilling of the sludge must be preceded by their stabilization in order to prevent the formation of lixiviates and biogas. Sludge landspreading is the best way for recycling the sludge of the sewage treatment plants. Effectively, in agriculture, this sludge is used as a fertilizer thanks to its high content in organic carbon, nitrogen and phosphor. Sludge landspreading of certain kinds of this sludge from sewage treatment plants, and which is full of heavy metals, may be a source of contamination for the receiving medium, at the surface as well as in depth, especially in the case of sandy soils [4]. When certain value limits of metal concentrations are achieved, utilizing this sludge in agriculture becomes impossible. The purpose of this study is to evaluate the metallic pollution and to determine its origin in order to preserve the sludge quality of Ibn Ziad sewage treatment plant of Constantine.

MATERIALS AND METHODS

The sludge samples were collected in the drying basins of the Ibn Ziad sewage treatment plant of Constantine. They were used after drying and crushing. The sampling was done in June 2014 and in January 2015 to observe the effect of abundant rainfall because it leads to the dilution of waste waters. This effect should be less significant on the quality of the sludge in the sewage treatment plants [5].

The evaluation of most present elements in the sludge was performed with X-ray fluorescence spectroscopy. This technique helps to make the list of all the elements of the Periodic Table except for hydrogen, lithium and beryllium. The analysis of the light elements (boron, carbon, nitrogen and oxygen) is tricky. As for the quantification of nitrogen and carbon, we carried out an extraction. Nitric nitrogen was dosed by UV-Vis spectroscopy, carbon by COD and acidity by *p*H-measuring.

The analysis by X-ray fluorescence was performed by Panalytical Epsilon 3 spectrometry of 9 watts power. Epsilon 3 is an energy dispersive X-ray fluorescence spectrophotometer for the elemental analysis range from Na to Am and concentration range from ppm to 100 %. The system is controlled by a computer equipped with analysis software OMNIAN. The sample is fitted under helium flux during analysis. The X-ray tube, which is metal-ceramic-made, ensures a better stability of the X-rays than the traditional glass tubes. It allows selecting optimal excitation conditions.

We recorded the X-ray fluorescence spectra four times under different excitation conditions (variable current and voltage). The use of a special filter with a tube voltage added to a particular tube current allows a better exploration of a particular region of the spectrum. The first spectrum was performed with a tube voltage 5.00 kV and a tube current 1000 µA. It allows the exploration of the area of energies reaching up to about 4 kV. The second spectrum was achieved with a filter made of silver that was 100 µm thick with a tube voltage 30.00 kV and a tube current 300 µA. It serves to see the high energy peaks. However, in such case, the peaks are highly weakened. The third spectrum was recorded with an aluminum filter of 50 µm thickness with a tube voltage 12.00 kV and a tube current 519 µA. The fourth spectrum was recorded with an aluminum filter of a 200 µm thickness with a tube voltage 20.00 kV tension and a tube current 450 µA. The use of the aluminum filter allows to explore the area of the spectrum between one and 20 kV. The decrease of the thickness of the filter allows to better check the low energy peaks.

An extraction was performed by agitation of 10 grams sludge in 100 mL ultrapure water for an hour. The solution obtained after centrifugation served for determining *p*H, COD and concentration in nitrate ions.

The measuring of *p*H was performed with a *p*H-meter JENWAY 3505.

The determination of COD was performed by energetic oxidation in sulfochromic medium of the organic matter. This induces a decrease of the initial concentration in potassium dichromate. The spectrometric dosing of the residual oxidant at 425 nm allowed us to determine the amount of oxygen necessary for the oxidation of the organic matter which is present in our sample. The oxidation was performed by COD-meter Hach model 45600 at 148°C. The UV-Vis absorbance at 425 nm was measured by using Hach DF/2000 spectrophotometer with 1 cm long quartz cell.

The determination of the nitrate concentration was performed after reacting the nitrate ions with sodium salicylate to obtain sodium paranitrosalicylate colored in yellow and could have spectrophotometry dosage at 420 nm. The measurement of optic density was achieved by UV-Vis spectrophotometer JENWAY with 1 cm long quartz cell.

RESULTS AND DISCUSSIONS

The X-ray fluorescence spectra under different conditions are represented on Figures 1 – 4. The position of the peaks tells us about the composition of the sludge. The qualitative analysis of the sludge shows the presence of the following elements: Ca, Si, Fe, Al, P, S, K, Mg, Ti, Cl, Zn, Sr, Ba, Zr, C, Cu, Mn, Pb, Cr, As, Ni, V, Br, Rb, Y, N, Se, Ga. This composition was not changed during our several samplings.

The sum of the masses of these elements represents 49.82 % of the sludge total mass. The presence of all these elements in the sludge from these sewage treatment plants as calcium for example is not an indicator of pollution. This is a consequence of their presence in the sewer that was treated by the sewage treatment plant [6].

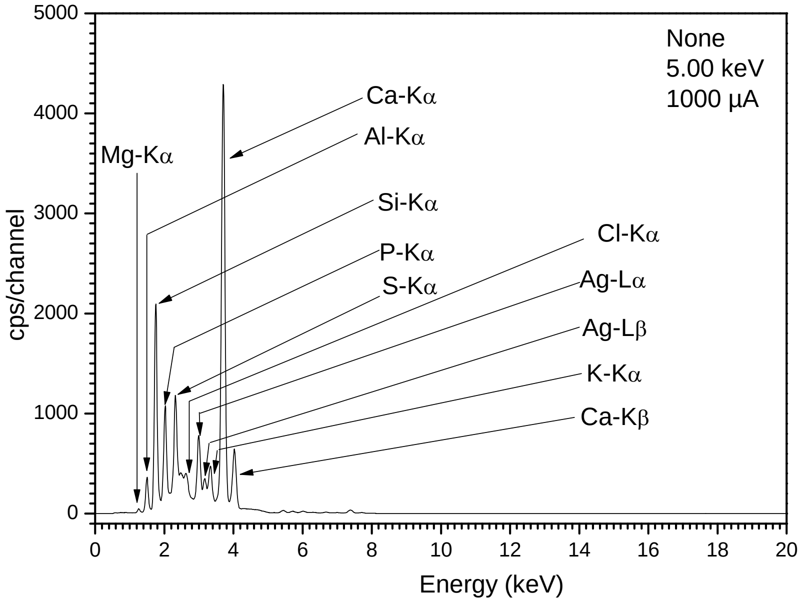

Figure 1. *XRF spectrum of sludge of Ibn Ziad Constantine wastewater treatment plant achieved without a filter, 5.00 kV, 1000 µA*

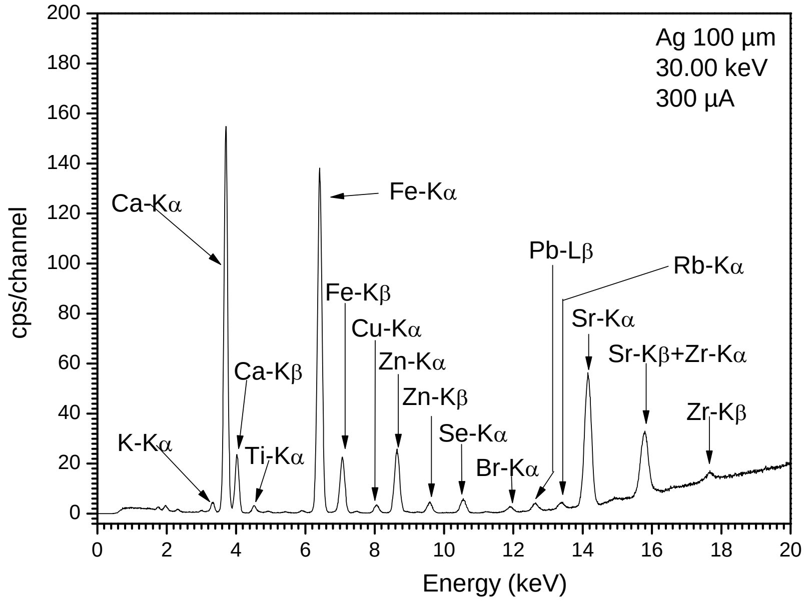

Figure 2. *XRF spectrum of sludge of Ibn Ziad Constantine wastewater treatment plant achieved with a silver filter of 100 µm, 30.00 kV, 300 µA*

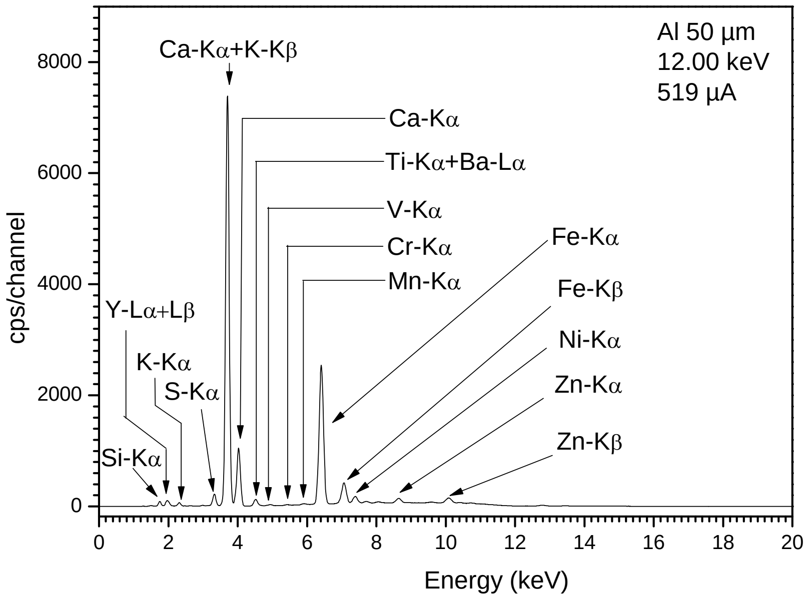

Figure 3. *XRF spectrum of sludge of Ibn Ziad Constantine wastewater treatment plant achieved with an aluminum filter of 50 µm thickness, 12.00 kV, 519 µA*

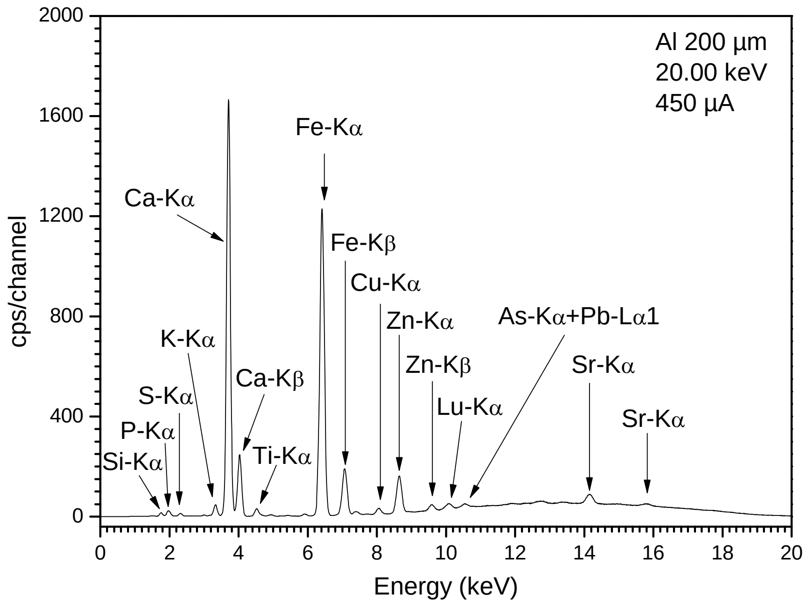

Figure 4. *XRF spectrum of sludge of Ibn Ziad Constantine wastewater treatment plant achieved with an aluminum filter of 200 µm thickness, 20.00 kV, 450 µA*

Certain trace metals are indispensable to cellular biology such as selenium, zinc, molybdenum, nickel, copper, and chromium. It is quite normal to find them in the sludge of the sewage treatment plant. These are metals which we find in the potable waters of the city of Constantine at very low concentrations [7]. In fact, the bacteria of the sewage treatment plants help them concentrate even more.

On the other hand, the presence of some other elements in the sludge is considered as pollution. This is the consequence of their presence in the urban sewers [8]. They are not biodegradable and remain in the environment. Their content in the sludge is limited by the regulations. The sludge is not allowed to be spread on the soils if a certain concentration of these elements is reached. We are also concerned with mitigating the concentration of these elements because the regulations also limit the flow of these elements in ten years Table 1.

Table 1. *Maximum levels of trace metals in sludge accepted to be spread permitted by the French Regulation [9]*

Trace elements	**Maximum permissible level [mg·kg^{-1} dry matter]**	**Maximum cumulative flow over 10 years [kg/ha/10 yrs]**
Cd	10*	0.15**
Cr	1000	15
Cu	1000	15
Hg	10	0.15
Ni	200	3
Pb	800	15
Zn	3000	45
Cr + Cu + Ni + Zn	4000	

* from 1st January 2004; ** from 1st January 2001.

The sludge that we studied was characterized by zinc, copper, lead, chromium and nickel pollution. During agricultural sludge landspreading according to the composition with clay minerals of the contaminated soils [10], some of these metals remained localized in the surface such as chromium. Others, as lead and nickel can migrate in the soil at speed 3 to 6 cm·year^{-1} and from 6 to 9 cm·year^{-1} respectively [4]. Their presence in the soils may not have any negative consequence on the plant growth [11].
We focused on the quantitative analysis of these metals. The peak height in the X-ray fluorescence spectra is dependent on the concentration of the metals contained in the samples. The concentration of the previous elements which are present in our sample is represented in Table 2.

Table 2. *Trace elements regulated present in the sludge of the Ibn Ziad sewage treatment plant of Constantine*

Compound	Zn	Cu	Pb	Cr	Ni
Concentration [mg·g^{-1}]	2.70	0.48	0.35	0.27	0.11

None of these concentrations exceeds the limit authorized by the regulations.
However the flow limit authorized over ten years in chromium, copper, nickel, lead and zinc is 15 kg·ha^{-1}, 15 kg·ha^{-1}, 3 kg·ha^{-1}, 15 kg·ha^{-1}, 45 kg·ha^{-1}, respectively, zinc being the limiting factor. Its concentration in the sludge is 2.70 mg·g^{-1} (2.77 kg·t^{-1}) and application is limited to an input lower than 45 kg·ha^{-1} over ten years. The sludge produced by the Ibn Ziad sewage treatment plant of Constantine can only be used with an amount lower than 16.6 t·ha^{-1} over ten years (1.66 t·ha^{-1}over 1 year). This quantity applied to the soils is insufficient to improve significantly the amount from the soil and the output of the crop. An amount of sludge no less than 25 t·ha^{-1}is indispensable for that [12].
The Ibn Ziad sewage treatment plant of Constantine can produce 18000 tons sludge per year. Complying with the sludge landspreading standards allows to use only

16.6 t·ha^{-1}. It will be necessary to use an area larger than 1084 ha for sludge landspreading. Even by following the former standards, pollution of the farming lands may nevertheless gradually occur [13, 14]. It is therefore necessary to reduce the pollution of the sludge of the Ibn Ziad sewage treatment plant in order to use it in agriculture. It will be necessary to control the industrial exhausts of the city of Constantine and address the possibility of disposing Zn, Ni, Cr, Cu, Pb in the urban sewers by an adequate biological treatment of the waste waters [8, 15 – 18].

Measuring the dissolved nitrate ion concentration provided us with a value of 0.12 mg·g^{-1} (0.12 kg·t^{-1}). If we apply 16.6 tons sludge per hectare, it will generate 1.99 kg ions nitrate per hectare. This amount of soluble nitrogen will be absorbed partly by the vegetation. The remainder will probably be degraded by the denitrifying bacteria located in the soil [19]. The risk that soluble ion nitrates may pollute the underground water table or the surface water is very limited.

Measuring the COD which provides the amount of soluble oxidizable material in the sludge has revealed a value of 0.45 mg·g^{-1} (0.45 kg·t^{-1}). This quantity is substantially composed of organic matters. If we apply 16.6 tons sludge per hectare, this will supply 7.47 kg soluble organic matter per hectare.

The measured *p*H of the sludge from the Ibn Ziad sewage treatment plant of Constantine is 7.1, which is harmless at landspreading.

CONCLUSION

The characterization by X-ray fluorescence of the Ibn Ziad Sewage treatment plant sludge allowed to demonstrate that it contains the following elements: Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Ba, Pb. Among the previously listed elements, there are chromium, copper, nickel, lead and zinc that have regulated content limit. They are present with the following concentrations, respectively: 0.27 mg·g^{-1}, 0.48 mg·g^{-1}, 0.11 mg·g^{-1}, 0.35 mg·g^{-1} and 2.70 mg·g^{-1}. None of these concentrations exceeds the limit authorized by the regulations. However the flow limit authorized over ten years in chromium, copper, nickel, lead and zinc is 15 kg·ha^{-1}, 15 kg·ha^{-1}, 3 kg·ha^{-1}, 15 kg·ha^{-1}, 45 kg·ha^{-1}, respectively. The sludge produced by the Ibn Ziad sewage treatment plant of Constantine can be used only with an amount lower than 16.6 tons over ten years (1.66 t·year^{-1}) while the needs in agriculture are higher than 25 tons per year. The sludge produced by the Ibn Ziad sewage treatment plant requires 10844 Ha for its landspreading. In order to reduce the size of this area, it will be necessary to better control the industrial wastes of the city of Constantine and examine the possibility to suppress Zn, Ni, Cr, Cu, Pb in the urban sewers by an appropriate biological treatment of waste water. The input of sludge landspreading from the Ibn Ziad sewage treatment plant with nitrates, organic matters and acidity seems not to be damaging to the environment.

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