REDOX COMPLEXATION OF MUNICIPAL SEWAGE SLUDGE (BIOSOLIDS) WITH NATURAL POLYPHENOLICS MOLECULES IN ALKALINE PH. THE CASE OF GALLIC ACID

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ABSTRACT

The degradation of water soluble extracellular polymeric substances (WS-EPS) of the activated sludge by complexation with natural polyphenolics such as gallic acid (GA) in alkaline pH under ambient O_2 and temperature is investigated. UV/Vis spectrum between 600 and 800nm wavelengths for (GA-EPS) complex, shows formation of new species which contain stable phenol-based p-type radicals, with pH-dependent concentration. In addition, the compositional evaluation of municipal sewage sludge by X-ray diffraction and thermogravimetric analysis (TG) shows (a) major diffraction peaks which appeared at 100ºC are attributed to the components $Mg_xCa_{1-x}(CO_3)$ *(x: 0.03-0.06),* $CaCO_3$, SiO_2 (quartz), $CaSO_4$ and $CaCl_2$ and (b) strongly complexation between inorganic and organic components in the sewage sludge, since organic components have been removed (at percentage 60%) at 550ºC temperature, as it was shown by the TGA analysis. Heavy metals like Cd, Cr, Co, Ni, Fe, Zn, Cu, Mn and Pb were identified by ICP-OES and were found in low concentrations.

Keywords: Sludge, Polyphenolics, Gallic acid, Redox, Free radicals, Degradation, Complexation, Extracellular Polymeric Substances (EPS)

1. Introduction

Today, sewage sludge landfill disposal is not ideal and there is now increasing incentive to economically develop viable reuse and recycling options [1]. A significant amount of research has investigated processing sewage sludge to form new materials such as compost [2]

The management of wastewater sludge, now often referred to as biosolids, accounts for a major portion of the cost of the wastewater treatment process and represents significant technical challenges [3]. In many wastewater treatment facilities, the bottleneck of the sludge handling system is the dewatering operation [4]. Advanced sludge treatment (AST) processes such as thermal and thermochemical processes [5], or chemical oxidation using hydrogen peroxide [6] have been developed in order to improve sludge dewatering and to facilitate handling and ultimate disposal. These methods degrade extracellular polymeric substances (EPS) proteins and polysaccharides reducing the EPS water retention properties [7]. The use of sludge, as a raw material for processing into new products such as compost requires the knowledge of the fundamental behaviour of properties and of components (organic and inorganic) of sewage sludge. Approximately 20% of the dry solids of sewage sludge is inert inorganic material and this forms the significant quantity of ash produced by sewage sludge incineration [8].

The Polyphenolics/Polyphenolics anion/Polyphenolics free radical triad ($PhOH/PhO^-/PhO^\bullet$) represents compounds that have great importance in a wide range of physicochemical and biological processes in humification [9-10]. The UV/Vis spectrum, of these couples in aqueous solutions, is strongly dependent on pH, redox potential E^o, Pb effect, numbers and position of

substituents on the phenolic ring. Substituents such as carboxyl (-COOH) and hydroxyl (-OH) groups on the phenol ring can significantly influence the electron density "*on the ring*" and thus modify UV/Vis spectrum dramatically. The UV/Vis spectrum of the PhOH governs the reaction of PhOH with O_2 to form free radical $PhO^{-\bullet}$[9-10]. At alkaline pH the pK_a 's of the PhOH are outstanding indicators of the electron density in the aromatic ring of the members of these triads (electrophilicity) and thus are excellent tools to predict half-cell reduction potentials for both the one-electron and two-electron couples, which in turn allow estimates of rate constants for the reactions of these triads.

The degradation of water soluble extracellular polymeric substances (EPS) of the activated sludge [7] by co-complexation with natural polyphenolics in alkaline pH under ambient O_2 is investigated. A molecular model which represents the above is the Gallic acid (GA, 3,4,5-trihydroxylbenzoic acid). GA is a natural polyphenol which exhibits the most considerable antioxidant capacity in plants and a successful model for the radical properties of natural humic acid with pKa 's 4.3 (carboxyl group) 8.8, 11.4, 11.7 (hydroxylic groups) and redox potentials E°<125mV (vs SHE) at pH>9 [9-10]. The (WS-EPS) and GA mixed, under ambient O_2 and temperature at alkaline pH. The redox mechanism degradation of (WS-EPS) is controlled by *UN-Vis* spectroscopy, *X-ray diffraction* and *thermogravimetric analysis* (TG) and by *physicochemical parameters*. This method suggests a novel role of natural polyphenolics on the degradation, dewatering and humification of aqueous wastes with a friendly interaction with the environment, as opposed to incineration of sludge.

2. Materials and methods

2.1. Experimental setup

Sewage sludge (Biosolids) at solid and liquid phase were collected from Naypaktos wastewater treatment station, in plastic bags and bottle respectively and brought to the field laboratory. Liquid phase Biosolids filtered through Whatman 113 (circles 110mm, cat No.1113110) paper and stored in a plastic bottle under refrigeration until use.

2.2. Reagents and solutions

All experiments were performed with analytical grade chemicals. Stock, working, and standard solutions were prepared with ultrapure water, Milli-Q water, produced by a Millipore Academic system (Millipore, Belford, MS). GA was obtained from Merck (purity > 98.5%, Nr. 842649) and used without further purification. GA stock solution in H2O (2mM) was prepared by dissolving 17mg of GA in 50mL of solution and stored in the dark at 4 °C. Standard solutions (Merck, Germany) were prepared by dilution of each pure element. The standard reference material of metals were used for the calibration and quality assurance for each metal. All aqueous solutions and dilutions were prepared with ultrapure water (Milli-Q, Millipore, Bedford, MA).

2.3. UV-Vis Spectroscopy. UV-Vis measurements were carried with a Hitachi U-1900 single beam UV-Vis instrument. For each sample, a dilute solution was analyzed across the UV-Vis spectrum to determine an appropriate wavelength for analysis. Samples where brought to the same pH value for measurement because light absorption by the studied organic acids can vary with protonation state and therefore pH. The simple analytical technique for the organic molecules used here has proven to be robust as well as rapid.

2.4. Single extraction of different metals from sludge

DTPA extractable fraction was obtained by mechanical shaking of sample (10g dry sludge) with 40 ml of 0.5 M DTPA, 0.01 M $CaCl_2$, 0.1 M TEA (triethanolamine) buffered at pH 7.3 for 2h at room temperature, according to Lindsay and Norvell (1978) [11].

2.5. Thermo gravimetric analysis (TG)

Thermogravimetric analysis (TG) provides an effective alternative to chemical analysis for the chemical characterization of sludges [12-13]. Thermogravimetric analysis (TG) of the dry sludge produced in Naypaktos treatment stations in Greece was carried out under nitrogen atmosphere (flow rate: 200 mL/min) in a PerkinElmer Diamond Thermogravimetric/ Differential Thermal

Analysis (TG/DTA) apparatus. A quantity of the sample (about 10 mg) was placed in a platinum pan at room temperature. Initially the temperature was raised at 100 °C and kept constant at this value until moisture removal and weight stabilization. After recording this weight as the initial one, the temperature was increased from 100°C to 800°C at a heating rate of 10 °C/min. The thermogravimetric (TG) curve were obtained by software.

2.6. X-ray powder diffraction (XRD)

The mineralogical composition of sludge was determined by XRD analysis [14-16]. X-ray diffraction analysis [14-16] was carried out using a model Bruker D8 Advance X-Ray diffractometer equipped with nickel-filtered Cu Ka (40 kV, 40 mA, λ = 1.5418 Å) radiation source. The step size and time per step were respectively fixed at 0.01º and 0.1 s, in the range of 5º ≤ 2θ ≤ 80º, to identify the crystalline mineral components of the sludge. X-ray patterns were interpreted by software.

2.7. ICP-OES Analysis of mineral elements

Microelement contents were determined in the DTPA extracts, using a Perkin-Elmer Optima 2100 DV optical emission spectrometer (Inductively Coupled Plasma-Optical Emission Spectroscopy ICP-OES) (Perkin-Elmer, Waltham, USA). In cases of high concentrations the samples were diluted 1:10.

2.8. Physico-chemical analyses

The determination of (%) moisture, pH, organic matter, conductivity (mS/cm) and (%) $CaCO_3$ content of the sludge was performed according to the Standard Methods for the Examination of Water and Wastewater of the American Public Health Association and AWWA [17]. The pH of the sample was measured in 1:3 soil water suspension using a Crison pH meter (Model GLP21); Electrical Conductivity (EC) was measured using Metrohm Conductivity meter (Model 712). Organic Carbon (OC) and Organic Matter (OM), are estimated by the method of Kalra and Maynard (1991) [18]

3. Results and discussion

3.1. Solid-Phase Studies

3.1.1. Physico-chemical evaluation of sewage sludge

Table 1: Basic physico-chemical properties of municipal sludge [20]

Test items	Moisture content (%)	pH	Organic matter (%) Burning at 230º	Conductivity mS/cm	$CaCO_3$ (%)
Test results	85±5	6.83 ± 0.01	22.6± 0.5	4.569± 0.001	12.9± 0.5

Table 2: DTP extractable heavy metals (mg/kg) in sewage sludge samples [20].

Metal	Fe	Zn	Cu	Mn	Cd	Cr	Co	Ni	Pb	Ref
Concentration (mg/Kg dry sludge)	211.7 ± 0.5	123.6 ± 0.5	73.7 ± 0.5	209.0 ± 0.5	0.261 ± 0.5	0.124 ± 0.5	0.424 ± 0.005	4.952 ± 0.005	18.5± 0.5	[20]
Limits total metals of sludge (mg/kg dry sludge)										
European legislation		2500-4000	1000-1750		20-40			300-400	750-1200	[21]
Greek legislation		2500-4000	1000-1750		20-40	10<		300-400	750-1200	[22]

The physico-chemical properties of municipal sludge from Naypaktos Wastewater Treatment station is shown in Table 1. According to Table 1 the content (%) of moisture of the sludge which is produced at Naypaktos wastewater treatment station was high. Thus, the application of sewage sludge to land requires an appropriate treatment with aim of reducing the percentage of moisture.

Considering commission Decision of 12 Julie 1986 and Greek legislation (1997) [19], the sewage sludge which is presented in Table 2 has heavy metal concentrations under the established limits. Although they are not legally restrictive, Co, Fe and Mn were in relatively low concentrations in the sludge analyzed, in order to allow its application to land (i.e., agricultural recycling) as soil retrieval material or as raw material in preparation compost.

3.1.2. Evaluation of complexation between inorganic and organic components in the sewage sludge by TG and XRD analyses

TG experiment was conducted to investigate the thermal stability of the samples, especially for determining the temperature above which the organic part of the sample is decomposed (Fig. 1). Figure 1 illustrates the TGA curve recorded for the digested sample.

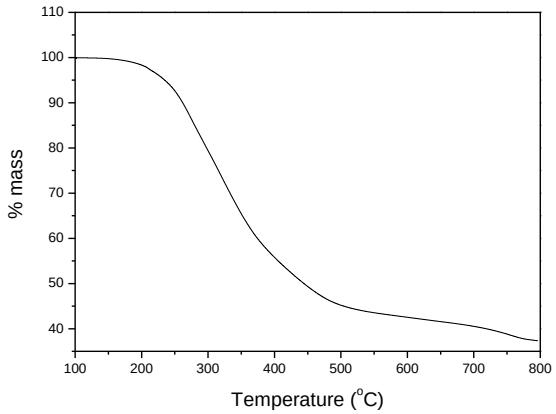

Figure 1: TG curve recorded for the digested sample of biosolids [20].

The curve shows that up to 200°C almost no weight loss is observed, whereas at higher temperatures a significant loss of weight is observed, which is almost completed at about 500-550°C. This weight loss is attributed to the removal of the organic part of the sample, which constitutes a large portion of the total sample weight, varying between 60% and 55%.
The X-ray diffraction peaks recorded in the 2θ range of 5–80 degrees for the digested sample of biosolids is given in Figure 2.

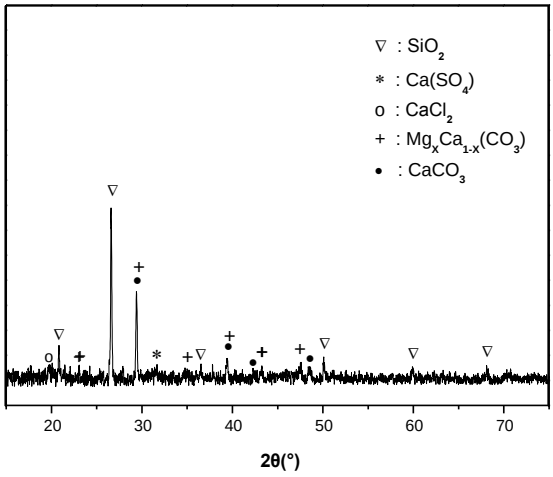

Figure 2: X-ray diffraction recorded in the 2θ range of 5–80 degrees, for the digested sample of biosolids [20].

In X-ray diffraction of the digested sample (Fig. 2), the main crystalline structures detected are the following: $Mg_xCa_{1-x}(CO_3)$ (x: 0.03-0.06), $CaCO_3$, SiO_2 (quartz), $CaSO_4$ and $CaCl_2$. All X-ray diffraction peaks should not be attributed to organic components, since these components have been removed in this calcination temperature, as it was shown by the TG curve (Fig 1).

3.2. Liquid-Phase Studies

The pH measurements of wastewater solution were carried out with a Hach Sensions1 pH meter and found to be 7.14.

3.2.1. UV/Vis Spectroscopy analysis

The UV/Vis spectrums for (A) Gallic acid, (B) Biosolids and (C) Gallic acid–Biosolids complex are given in Figure 3, *after one*-half hour incubation at pH>9.

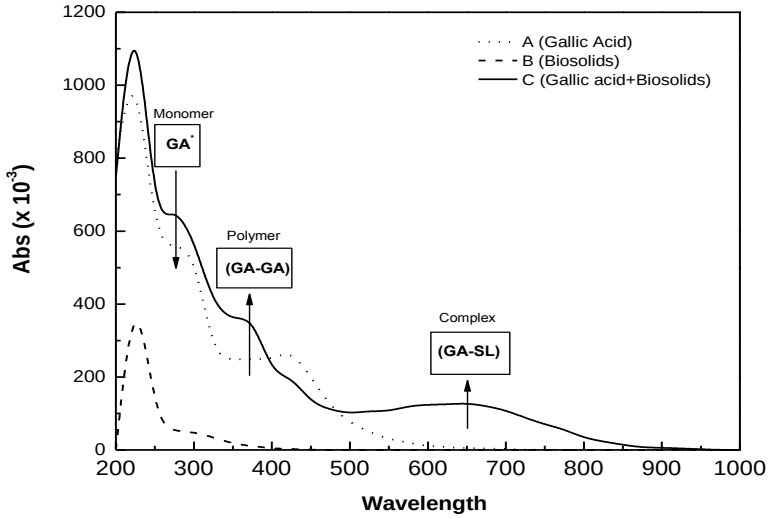

Figure 3: UV/Vis spectrum for (A) Gallic acid (GA), (B) Water soluble Biosolids (SL) and (C) Complex Gallic acid–Biosolids (GA-SL) at pH>9.

Gallic acid (GA) Spectrum

According to Fig. 3A, the UV/Vis Spectum for GA solution concentration 100μM, extends from 200nm to 600nm wavelength. For short times, peaks near 225nm and 280nm appear in the spectrum. By increasing the time these peaks decreased while a new peak appeared at 430nm wavelength. At prolonged time the peak at 430nm appeared an horizontal plateau between 450nm and 350nm wavelength. The above is evidence of the existence of a reactant and a product species in the solution. So, according to previous studies [9-10], we suggest the following polymerization reaction (eq-1) for GA solution:

$$(GA^{\bullet})_{280nm} \rightarrow (GA\text{-}GA)_{(350nm\ to\ 430nm)} \quad (1)$$

Biosolids (SL) Spectrum

According to Fig. 3B the UV/Vis spectrum for biosolids solution extends from 200nm to 300nm wavelength with a maximum around 225nm which maintained at prolonged accumulation time.

Gallic acid–Biosolids (GA-SL) complex spectrum

According to Fig. 4C, the *(GA-SL)* spectrum extends from 200nm to 900nm wavelength. For short time, peaks near 225nm, 280nm and 380nm wavelength appear in the spectrum. By increasing the time these peaks decreased while a new peak at 650nm wavelength increased dramatically with time. At prolonged time the peaks at 280nm and 380nm appear an horizontal plateau.

3.2.2. Redox degradation mechanism of Biosolids by free radicals

As shown in a spectrophotometric study at pH>7, GA and its analogues are rapidly oxidised by atmospheric oxygen [23] Electron paramagnetic resonance (EPR) spectroscopy showed that, at alkaline pH greater than 8, gallic acid (GA) can form stable radicals whose pH dependence and spectral features are similar to those observed in humic acid under similar conditions. This EPR signal is characteristic of phenolic p-type radicals and bears strong resemblance to the indigenous radicals of natural Humic acid [9]. Accordingly, we suggest the following steps of solution reaction between free radical GA and SL

$$(GA^{\bullet})_{280nm} + (SL) \rightarrow (GA\text{-}GA)_{(350nm\ to\ 390nm)} + (GA\text{-}SL)_{(650nm)} \quad (2)$$

These findings point to the need for a more systematic study of the complexation of these organics on biosolids, with specific attention not only on the complex process but also on other important issues such as free radical physical chemistry and the possible synergistic role of metal ions such as Pb.

4. Conclusions

The interaction of polyphenolic molecules such as gallic acid with the biosolids liquid phase is a complex process involving adsorption and redox reactions. A comparative analysis for GA, SL and GA-SL reveals that the UV/Vis spectrums correspond to distinct reactions. These can be assigned to complexation of gallic acid with a part molecules of the water soluble extracellular polymeric substances of biosolids by free radicals mechanism. So, this mechanism shows the degradation of the extracellular polymeric substances of biosolids in simplest polymeric substances.

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