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Microwave Digestion of Hazardous Waste Sludge in Geothermal Hot Waters by Char/Fly Ash Granule Composts-Hazardous Sludges and Industrial Waste Water Treatment

Yıldırım İsmail Tosun

Abstract

Most of the previous were regarding characteristics of sludge from urban/municipal activities concerning environmental issues on industrial sludge discharges causing fatal disasters in the lakes and water streams. The washing treatment of mud was searched. This research study concentrated over oxidative heavy metal dissolution and sterilization washing of muddy sludge of chemical, steel and copper refinery plants. The hazardous Hg and Pd contents using washing dissolution provided recovery of metals and treated sludge as the feedstock for digestion process. The research used hazardous sludge which is the by-product of the heat treated steel manufacturing process of CN baths and sludge from pulp washing industries. However, there is a sterilization washing by microwave radiation was reported on various sludge metal contamination characteristics in wastewater treatment stage. The results of a limited number of bench-scale sludge washing experiments conducted in the tube reactor study confirmed high radiation trends for washing dissolution with H₂O₂ in soil samples obtained from different locations in the north lake area of discharge of at the Plant Site. In general the contaminants in waste pond soils partitioned preferentially to the fine fraction of the soil (<150 µm however, the sand fraction (–0,5 mm + 150 µm) still contained significant contamination. These tests also showed that the heavy metal contaminants were highly dissolved at 45–76% in the wash water, which will reduce washing toxicity and improve metal recovers.

Keywords: fly ash, microwave radiation, salt slurries, metal sorption, energy toxic risk assessment, stochastic cost estimation, treatment sorbent simulation, hybrid sorbent, waste sludge, salt slurries, Microwave activation waste water treatment, heavy metal, fly ash composts, shale

1. Introduction

All of the individual domestic wastewater streams contribute different amounts to the total nutrient and element potential beneficial to plant and farming. The contaminating seepages to streams should be control by local governors including the discharged areas for wastewater. However, industrial wastewater is commonly defined as wastewater from dairy factories, cheese factories, nut mills, pulp, paper, petrochemical flow, as well as industrial wastes such as various chemicals, salts and tanning acids, mining leachates. These sources vary widely in composition and often require special teritoriary processes to comply with discharge regulations. The simulation of hydrological flow discharge and fresh water wells and seepage contacts with irrigations is critical for agricultural farming and urbanization. The geothermal hot waters near Tigris River and even sulphide ore seepages, waste leachates of gold mining may deteriorate fresh water sources and agricultural land in the local area. Theuse of geothermal waters for precipitation of contaminated effluents with neutralizationh will protect the environment and agricultural fields in the South Eastern Anotalian region. The chemical analysis of the geothermal waters and given in **Table 1** [1]. The rivers, stream and flow waters in the South Eastern Anotalian region with contaminated area are illustrated in **Figure 1**.

Hazardous digestion of sludge tends to occur highly common as industrial waste streams or seepage, dissolved matters resulting from tanning or mining material oxidation of toxic species, react with geothermal bicarbonate and producing a strong hydroxyl precipitates, also neutralize the alkalinity of waste water streams as given in Eqs. (1)–(3). The basic alkali matter of geothermal waters may neutralize the acidic waste streams in production at higher pH levels over 5 with digested heavy metals in sulphide minerals. The neutralization by alkali matters govern the toxic seepage control by precipitation reactions in geothermal hot saline waters containing ammonia and bicarbonate as given below;

Derince Çayı	BATMAN
Batman Çayı	BATMAN
Dicle Nehri	BATMAN
Yanarsu Çayı (Garzan Çayı)	BATMAN
Dicle Nehri	BATMAN
Bitlis Çayı	SİİRT
Sutopu Deresi	BİTLİS
Ulu Çay (Botan Çayı)	SİİRT
Ulu Çay (Botan Çayı)	SİİRT
Dicle Nehri	SİİRT
Dicle Nehri	SİRNAK
Yukarısaksan Deresi	SİRNAK
Çığlı Suyu(Zap Suyu)	VAN
Çığlı Suyu(Zap Suyu)	HAKKARİ
Şemdinli Çayı	HAKKARİ

Table 1.
The streams and ground water area in the Şırnak, Batman and south eastern region [1, 2].

Figure 1. Satellite view of precise and geothermal water areas in South eastern Anatolia, Euphrate and Tigris Zone [2].

Bicarbonate and sulfite hot waters fall pH and hydrolysis as below.

The sulfide matteris highly reactive to heavy metals as given Eqs. (2) and (4):

which form very stable sulfide metals. The further reaction is an oxidation of S^{2-} to S^- , as given in Eq. (6):

generated in the late muds close to the settled mud - water interface. ZnS and PbS, in the soil are much stable and gives oxidation S in the -2 state to effluent. However, the sulfate part of reaction (2–3) may cause redox effect an oxidation. Then

The oxidation electropotential matter of waste waters provides toxic heavy metal dissociation to stream seepages near the mining leaching area. The geothermal waters provide the hydroxide precipitates in solid matter as mud. Even jarosite precipitates by sulfihite rich geothermal hot water streams area showing an output view in the land as redish brownish colors. However, the land may become dangareous with higher heavy metal contamination for fish farming and stream fishing. Batman province copper and lead sulphide deposits and hot streams of high

sulphate come out high nitrate potential contamination of fresh waters soueces as given in **Figures 1** and **2** [2].

Some of the drinking water needs of Siirt Center, Kurtalan, Tillo (Aydınlar) Districts and Kayabağlar, Gökçebağ and Atabağı Districts are provided by natural spring water called Hesko in the countryside of Şirvan District and caisson wells on Botan Stream. In addition, there are underground water drillings for agricultural purposes, water drillings opened to meet the utility water needs of individual industrial facilities, and many water drillings with or without registration (without groundwater usage permit) in rural (villages) to meet the utility and drinking water needs. There are two healing geothermal springs in the province, namely the Sağlar (Billoris) Hot Spring at 15 km on the Siirt-Eruh Road and the Fiber Spa at the banks of the Reşan Stream in the Kışlacık Village.

Wastewater arises in Şırnak as any rainwater runoff, as well as coal mining and geothermal hot saline discharge, domestic or commercial wastewater acidic seepage or any combination of these carried by sludge to fresh water resources. The type of wastewater generated is changed by both the population and the combination of geothermal seepage surrounding, domestic industrial activities. Hazardous sludge affect the discharge patterns as well as the fresh water chemical condition. The wastewater management need efficient waste treatment system. The proper identification and characterization of the contents entering a wastewater treatment plant is essential. This is based on the physical, chemical and biological properties of the flow; on the receiving environment where the treated wastewater will be discharged. The direct and subsequent impacts are important, as well as the environmental and discharge standards already established. Four main types of wastewater can be listed as domestic, industrial, agricultural and urban. Urban wastewater is defined as a combination of domestic and industrial wastewater, as well as environmental wastewater infiltration and rainwater, while agricultural

Figure 2.

Euphrate - Tigris Basin nitrate sensitive ground water areas and ground water flow areas.

wastewater consists of wastewater obtained from processes from surrounding farms, agricultural activities and sometimes polluted groundwater. **Tables 2 and 3** showed the parameter values permitted in the region in which high agricultural wheat fields, cattle and fish farming are affected by ground water change and contamination regarding to legislative precautions [3, 4].

Generally, the main contamination occurs mainly on domestic and industrial sewage, where plants are affected and the source of contamination. However, the agricultural irrigation and farming chemicals is becoming increasingly important due to the high amount of use pesticides and fertilizers in agricultural fields especially dry stony lands exhausted by high amount remnant chemical toxic matters in the land. The composition of industrial wastewater varies according to the type of environmental industry, with the pollutant and pollutant composition related to the general classification into inorganic and organic industrial wastewater [5–10]. Wastewater was directly discharged to the sea water surfaces for a long time as a result of the dislocations of many stream discharge structures and the land deterioration of the discharge transmission pipes, which is completely crossed from the Şırnak.

Raw wastewater in Şırnak due to coal mining quarry creates a risk if these systems fail and the suspended sludge wastewater becomes more difficult to treat. There is no technical and technological relationship between the collection of wastewater through the sewerage network, its transmission to decantation, its treatment and discharge. Therefore, compliance with the criteria of projecting in neutralization and decantation added to the end of the sewage is very weak and non-existent. Thus, current and future technologies will eventually have to deal with mining leachate area and tailing pond areas such as the following control mechanisms [11–22]:

- water decantation treatment and neutralization recycling;
- precipitation heavy and/or precious metals, anions, adsorption residual organic chemicals, complexes or chelates;
- oxidation cyanide and arsenic without destruction;
- collection oil spills, separation by solvent extraction liquors
- precipitation neutralizing of acidic mine waters which is certain amounts of base metals such as copper, zinc, lead in addition to ferric iron and sulfate;

Discharge Parameter, unit	Composite sample, 2 hours	Composite Sample, 24 hours
Chemical oxygen requirement (COD)(mg/L)	250	100
Oil and grease(mg/L)	20	10
Ammonium nitrogen (NH ₄ -N)(mg/L)	150	100
Chrome (Cr + 6)(mg/L)	0.5	0.5
Lead (Pb)(mg/L)	2	1
Total cyanide (CN ⁻)(mg/L)	0.5	0.1
pH	6–9	6–9

Table 2.
The discharge legislation (RG-13/2/2008-26786) values for waste water treatment plant's discharge of spare parts, machine manufacturing, electric machines and equipment [3, 4].

Parameter	Sewerage systems in wastewater infrastructure results with full treatment	Sewage systems in wastewater infrastructure facilities resulting by deep sea discharge
Temperature (°C)	40	40
pH	6.5–10.0	6.0–10.0
Suspended solid (mg/L)	500	350
Oil and grease (mg/L)	250	50
Tar and petroleum based oils (mg/L)	50	10
Chemical oxygen demand (COD) (mg/L)	4000	600
Biochemical Oxygen Demand (BOD5) (mg/L)	—	400
Sulphate (SO4 =) (mg/L)	1700	1700
Total sulfur (S) (mg/L)	2	2
Phenol (mg/L)	20	10
Free chlorine (mg/L)	5	5
Total nitrogen (N) (mg/L)	—	(a) 40
Total phosphorus (P) (mg/L)	—	(a) 10
Arsenic (As) (mg/L)	3	10
Total cyanide (Total CN ⁻) (mg/L)	10	10
Total lead (Pb) (mg/L)	3	3
Total cadmium (Cd) (mg/L)	2	2
Total chromium (Cr) (mg/L)	5	5
Total mercury (Hg) (mg/L)	0.2	0.2
Total copper (Cu) (mg/L)	2	2
Total nickel (Ni) (mg/L)	5	5
Total zinc (Zn) (mg/L)	10	10 Total tin (Sn) (mg/L)
Total silver (Ag) (mg/L)	5	5
Cl ⁻ (Chloride) (mg/L)	10000	—
Surfactants (MBAS) reacting with methylene blue (mg/L)	Not involved	Not involved
(a) These parameters will not be taken into account in wastewater evaluation. b) For strong organic wastewater containing more than 2% inert COD and a total COD value of more than 5000 mg/L, the BOD5 value is taken as basis instead of COD.		

Table 3.
The discharge parameter values at environmental legislation (RG-13/2/2008-26786) for wastewater regarding Turkish standards intended for discharging wastewater to wastewater infrastructure [4].

- absorption control of residual effluent matters in flotation such as frothers, flotation collectors and modifiers (activators or depressing agents, pH regulators);
- precipitaion pasting of radioactive waste waters,
- decantation control in aqueous effluents and soils [7, 8].

Groundwater can be contaminated by the failure of on-site wastewater systems that can contaminate nearby water sources and wells. One way community work to protect the health of the public is to establish a very good concurrent management program for on-site wastewater treatment systems. The idea behind these programs is to assist homeowners by monitoring and managing centralized systems to make sure they are always working correctly and that the health of the community is never at risk.

In this research, prospected tests that the formation of Fe^{3+} by geothermal ozon reactivity on the oxidation Fe^{3+} surface in turn forms CN, AsO^{-3} , OH^{-} complexes [8, 11]:

The As (III) oxidation reaction then proceeds as Eq. (6)

Toxic intermediates may be sorped by char and shale clay may be generated as neutralization and precipitation heavy metals as organic complexes from this geothermal digestion technique. Also, the barrier-integrity verification, effective emplacement of barriers and modeling were found to be quiet difficult [13–15].

The dissolution kinetics of soil mud particle for Cr heavy metal is followed by equation

$$\frac{dc_{\text{CrO}4}}{dt} = k_i e^{-t/c} \quad (10)$$

Where CN, AsO_3 contamination mg/l, k the rate of dissolution of ciyanide and chromate, i is the reaction style, t is time,

The digested soil mud and accumulated metal in effluent of lake streams as regarding contamination is followed by equation, where n is kinetic order type

$$\frac{dc_{\text{AsO}3}}{dt} = k_i c^{tin} \quad (11)$$

The saturation amount affect digested level of toxic CN concentration. The accumulated effluent activity of oxygen and oxidation reactions of hot water streams as precipitates metals and even iron cyanide chealates in contaminated streams. The sulfite and sulphate hot waters react as followed by equation, where SO_4^{-2} sulphate and sulfite concentration in effluent, f_i is concentration rate of sulphate in total effluent

$$\frac{dc_{\text{Pb}}}{dt} = k_i c^{tin} . dc . f_i (\text{SO}_4^{-2})^{tin} \quad (12)$$

The dissolution concentration of accumulated metal in aliquate of limestone rocks dissolution by hot water streams in subground lakes with high CO₂ gas dissolved streams as regarding Pb heavy metal contamination is followed by equation, where HCO_3^{-2} bicarbonate concentration in effluent

$$\frac{dc_{Pb}}{dt} = k_i c^{tin} .dc.f_i (HCO_3^{-2})^{tin} \tag{13}$$

The digested soil mud and heavy metal in effluentof high fertilizer digestion by wrong amount of fertilizer use in farming discharges to fresh water streams as decayed mud with lack of COD and Pb heavy metal contamination is followed by equation, where HNO_3^{-2} nitrate concentration in effluent

$$\frac{dc_{Pb}}{dt} = k_i c^{tin} .dc.f_i (HNO_3^{-2})^{tin} \tag{14}$$

Fish farming in the lakes and streams in the region require lower concentrations for breeding below 1 mg/l Pb Cu and Cd and Zn in contact to basaltic rocks and sulphide matter near copper ore deposits. The water could monthly oxidize slightly surfaces of sulfides resulting in seepages contained highly around %1–2 Pb and 200mgCu at high attitude deposits in Siirt and Şırnak. Even gold mining heap

Effluent, mg/l	Şırnak Coal Mine Pool	Şırnak, Hezil Stream	Güçlükonak Hot Stream	Batman Hot Stream	Şırnak Kasrik Laguun	İlisu Dam Laguun1	İlisu Dam Laguun2
Hg	8,11	4,71	12,3	14,11	4,71	4,71	4,71
Pb	10,58	14,53	23,2	12,58	11,53	5,7	5,2
Fe	40,33	70,62	59	93,3	56,2	60,62	67,62
K + Na	7,52	8,46	8,7	8,52	8,6	≥70	≥50
Cd	24,72	19,56	14,1	14,72	19,56	16	15
Mn	33,3	24,1	24,2	43,3	24,1	≤25	≤25
Cu	27,2	30,2	15,7	7,2	10,2	≤15	≤15
As	1,10	2,44	2,8	2,10	2,44	≤5	≤5
SO ₄	0,57	0,37	1,9	0,67	0,55	≤15	≤15
Soil, ppm							
Hg	34,11	48,71	52,3	54,11	40,71		
Pb	10,58	24,53	23,2	20,58	11,53		
Fe	4,33	7,62	5,9	9,33	5,62		
K + Na	74,52	81,46	81,7	84,52	88,6	≥70	≥50
Cd	24,72	9,56	10,1	4,72	19,56		
Mn	2,72	3,02	1,5	0,72	1,02	≤5	≤5
Cu	3,33	2,41	2,4	4,33	2,41	≤5	≤5
As	1,10	2,44	2,8	2,10	2,44		
SO ₄	0,57	0,37	1,9	0,67	0,55		

Table 4.
Şırnak and Batman province reveals the potential geothermal hot waters and contaminated soil.

Biosorbent	Co (mg L ⁻¹)	te(exp) (min)	qe(exp) (mg g ⁻¹)
Rice husk	5–300	150	17.87
Wheat shell	250	120	10.84
Pine cone powder	120	15	19.02
Tea leaves	20	30	62.80
Sawdust	10	30	1.50
Seed powder	10	30	4.82

Table 5.
Equilibrium time for Cu adsorption capacities studied with different biosorbents.

leachates also leaks to ground water streams by flooding [15, 16]. The contamination of some accumulated heavy metal contents of hot streams and soils in the region are given in **Table 4** [22, 23].

The geothermal saline water digestion approach is based on washing the entire sludge and fluid that extracts the contaminants from all size fractions. The pilot microwave digestion and geothermal hot water assisted sludge decantation techniques is used flocculants, polyelectrolytes, chelants, inorganic acids, or surfactants depending on site.

The industrial waste water cleaning areas, non-burning, slippery to create a safe working environment absorbant fly ash is used. In the waste water treatment, the amount of fly ash used for hazardous waste water treatment is more than 180,000 tons/year. The sorbent matter variation may eliminate the contaminated effluent levels at equilibrium ambient concentrations given in **Table 5** [9].

Heavy metal containing mud or with lack of COD and scarcity of water forces to control fresh water resorces by using decantation and neutralization with adsorbants such as clay in the chemical industry and in tanning discharges [6–9]. The clay, fly ash and sepiolite is good absorbant [10–14]. The activated bentonite or montmorillonite is good sorbent for fresh fruit drinks and brewery, water tretmeants in Europe [15–19]. The use of clay is exceeded 2 million tons/year in the world waste water treatment [20–21]. The fly ash is stable in neutralization on the layered clay cages at hot stream temperatures [22–28]. This research work was carried out on geothermal hot waters and microwave radiated digestion of waste waters in Şırnak for heavy metal sorption and reduction. In this study, fly ash, char, shale and marly shale of Şırnak and absorbant properties, was improved by saline water digestion. Fly ash and char absorbance by cavity passing through certain bed properties was performed and the absorbance was measured at the mechanical strength change has been studied.

2. Material and methods

2.1 Fly ash - char compost with Geothermal water digestion

The geothermal water digestion technique digests the hazardous species and reduces the amount of metal content in sludge [29],
In this study, the effect of water quality) was subjected to the concentration and further alkali activation tests with mixed type The geothermal water quality on concentration and alkali activation were declared based on the pH, CEC (Cation exchange capacity), sludge viscosity (**Table 6**).

Sorbent Type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	CaO	MnO	LOI*
Zeolite (%)	47.85	24.30	0.32	1.7	0.77	2.7	0.10	10.27
Şirnak Asphaltite Char Shale	27.50	7.70	10.83	2.17	1.97	10.5	1.74	5.47
Bentonite	50.45	17.80	6.83	12.17	4.97	3.57	0.20	7.37
Marly Shale	17.85	11.60	0.83	5.17	3.97	20.57	0.40	5.27
Fly ash	27.80	13.60	17.83	4.17	2.97	10.70	1.50	16.27

*LOI: Loss on Ignition at 1000°

Table 6.
Sorbent types for washing treatment.

2.2 Microwave digestion and heavy metal sorption

Microwave assisted organic reactions hydration, synthesis of complexing chelates by alkali matters in clays and geothermal waters. The fly ash content: $2\text{MgFe Si}_8\text{O}_{20} (\text{OH})_4$. The chlorite, aqueous magnesium, aluminum silicate. Sepiolite is $6\text{Mg}_9 \text{Si}_{12}\text{O}_{30}(\text{OH})_4 \cdot 6\text{H}_2\text{O}$ group is hydrolized Mg silicate. The pore water is scarcely bound to crystal sliding layer of magnesia and hydroxyl base. Fly ash and clay minerals under microwave radiation is heated easily [10]. Microwave digestion could activate digestion use as heating as studied in this study over slurries illustrated in **Figure 3**.

2.3 Sorbent clay/oak wood char - waste sludge

Clay minerals are used as activated, compositions are closely dehydrated. The particle size, particle shape, surface chemistry, ion exchange capacity, color, etching, viscosity, plasticity, sorption ion, adsorption surface are the main parameters in waste water treatment [30–39]. The properties of clay minerals significantly impact on the use of. Absorption can be carried out in the presence of water or other liquid the pores of the mass (solid material) [40–44]. Absorbents material in waste water and other chelates is a sponge sorbent as material containing pores adsorp the contaminating heavy metals and cyanide durings neutralization affect [45–49] (**Figure 4**).

Figure 3.
Microwave radiation heating for waste water digestion.

Figure 4.
The micro pictures Şırnak marly shale char shale as sorbent.

Sorbent	Bulk Density, kg/cm3	Porosity, %
Shale chlorite	800–980	45
Şırnak Coal Char	530	66
Oak wood char	220	78
Silopi fly ash	700	33

Table 7.
Shale and Marly shale and fly ash properties.

	Specific gravity, g/cm ³	Specific surface area, m ² /g	Micro porosity, %
Zeolite (%)	2,56	34	44
Şırnak Asphaltite Char Shale	2,03	45	32
Bentonite	2,62	32	66
Marly Shale	2,71	11	12
Fly ash	2.23	67	47

Table 8.
The chemical properties of different sorbents and Şırnak shale and Marly shale and fly ash used in neutralization and adsorption treatment.

Component	Güçlü Konak 1 (mg/L)	Çermik (mg/L)	Batman 3 (mg/L)	Beytüşebap (mg/L)	St (mg/L)	Ya (mg/L)
Ca2+	55	222	17	953	3760	221,40
Fe2+	0.1	n.d.**	n.d.	n.d.	n.d.	834
K+	6.1	6.4	5.0	97.2	430	1370
Mg2+	10	33	6.1	276.8	1270	2860
Mn2+	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Na +	15	109	365	16,785	90,100	94,900
F ⁻	0.3	0.5	0.5	n.d.	n.d.	n.d.
Cl ⁻	19	121	310	27,541	14,300	18,000
NO3 ⁻	1.3	114	0.9	n.d.	n.d.	n.d.
SO4 ²⁻	13	250	14	1132	3600	283
HCO3 ⁻	210	502	512	185.4	40	67

Table 9.
The chemical composition of geothermal hot waters in Şırnak and Batman [1, 2].

2.4 Fly ash/Asphaltite shale char composite

This compost is especially sorbent used waste water treatment. The fly ash compost granules use as hazardous industrial waste waters and the sorbent types and desirable properties of activated and cleaned sorbents in the experiments are given in **Table 7** and chemistry are given in **Table 8** for geothermal waters used in neutralization (**Table 9**).

Material to be used as powder is packed distributed in tube bed permeable granule grain size, basic as absorption capacity by the cat should be accepted. High absorption capacity having fly ash should avoid digestion waste waters passed through cavities. The grain size distribution of sorbent granules is important and between 1 and 6 mm. The sorbent beds are rounded surfaces not to create dust mass transport during mechanical stick and fouling cavity.

3. Results and discussion

3.1 Neutralization decantation and precipitation

High salt content in the hot brines may deteriorate electrolyte potential at low levels. The dissolved silisium contents may even bound bicarbonate and calcium rective component. Low level salt contents of Şırnak and Batman province will be highly advantageous for precipitation of heavy metals and metal cyanides (**Figure 5**).

3.2 Microwave digestion with geothermal water- washing

The required ozone dosage depends on a number of factors, most notably the type of wastewater treated. The Şırnak solid wastes can threaten surface water and groundwater resources. Strategies are needed to identify and solve local pollution

Figure 5.
The composite sorbent use, Fly ash distribution in salt hydration under microwave radiation.

Figure 6.
 Schematic view of an washing with microwave recycled by microwave sorption technique.

problems, and residents, businesses and industry need to be educated about the health hazards associated with untreated wastewater. Safe drinking water and proper treatment have been recognized as indispensable factors for sustaining life. Increasing poverty is exacerbated by factors such as increasing population growth and rapid urbanization, as well as hydrological variability and climate change. These socio-economic and environmental factors come about by increasingly valuing water and wastewater infrastructure. Reliable wastewater treatment systems serve together with the degree and quality of the wastewater, which determines the effects of these treatment plants on the environmental water resources released, as a good indicator of the level of development in municipal and public health. In the last few years, the amount of municipal wastewater generated has increased significantly due to the steady increase in the population with increasing dependence on decreasing water resources (Figure 6).

3.3 Char carbon compost washing technology - sorbent applications

The slurries is stand for 30 minutes after being conditioned. At the end of the period, the settled mud was removed by decantation method and dried.

The effluent by adding salts at concentrations ranging from 30,125 ppm to 1000 ppm, until the precipitates were obtained in sufficient quantities with pure water in the waste water.

The step wise washing cycle is practised in the geothermal waste water slurry: there is no water-effluent washing column unit connected to the waste sludge, and the washing sorbent bed contained one single microwave radiation column is used to wash in the three decantation washing norms: roughing, scraping and cleaning. The variation of the third cycle washing is also slowed recycling by microwave act.

The simple production presented as adapted and optimized depending on the target application. The main applications are briefly described in the following sections. Although this review only focuses on state-of-the art commercially available pellet plants, it should be noted that some prospective advanced applications for heat melting of binder are currently being studied, mainly in the form of prototypes or proof-of-concepts. These innovative applications include:

- Compost systems, in which the extrusion mold system takes advantage of temperature gradients in wet gradient.
- Compression press systems, where the high load press is used to drive the forming sludge in plant.

- Continuous conversion systems, utilizing the high temperature binding gradients 75°C and amounts (of at least 200°C) in slurries to drive a recycle.
- Hot production, where the scraping power of the load system is used to drive the compressive form of hot system.

3.4 Langmuir absorption model by hot water streams

Langmuir and Freundlich concentrations for As(V) adsorption onto sorbent at different temperatures Non-linear pseudo-first-order [11–12]:

$$qt = q_{e,1} \left(1 - e^{-k_1 t}\right) \tag{15}$$

Non-linear pseudo-second-order:

$$qt = \frac{qe^2kt}{1 + qekt} \tag{16}$$

Linear pseudo-second-order:

$$\frac{1}{qt} = \frac{1}{kqe} + \frac{1}{qe^2} \tag{17}$$

For an overview of these more innovative and prospective applications, the general common method can be given in **Tables 10** and **11**.

it is found that the amounts of neutralization ions is hydrated and formed in the mud at higher microwave temperatures with even the H + ions. Mg, and Fe atoms in the octahedral clay layers and the Al atoms in the octahedral centers manage stable porous sorbent compost, as well as the Al atoms in the tetrahedral layer, as well as Al₂O₃, MgO and Fe₂O₃.

The first order sorption concentration at three stage cycling counted by the equation regarding the phosphate sulfite, and nitrate concentrations in the waste waters as studied stepwise concentration weight increase determined by weight regressed exponential rate change as given below:

Run,	C, mg/l	k ₁	a	b
1	28	0,3	0,15	1,2
2	20	0,24	0,22	1,7
3	12	0,21	0,27	2,4

Table 10.
The activated bentonite compost with char shale of Şırnak materials.

Run,	C, mg/l	k ₁	a	b
1	28	0,3	0,15	1,2
2	20	0,24	0,22	1,7
3	12	0,21	0,27	2,4

Table 11.
The activated fly ash compost with char shale of Şırnak materials.

$$\ln c_{Pb}^{NO_3,PO_3,S_2O_3} = 1 + \frac{k_{NO_3}t}{1!} + \frac{k_{PO_3}t^2}{2!} + \frac{k_{S_2O_3}t^3}{3!}, 3ppm < c < 300ppm \quad (18)$$

Cation exchange ability of clay was so effective parameter in metal sorption manner. The alkali pH provided efficient washing criteria in the column sorption.

It is illustrated in the **Figure 7**, the lower pH decreases inversely limiting sorption and reduce the amount of neutralizing salt added to oak wood char sorbent. When FeCl₃ is used, iron ion fouling is observed in the sorption with coal char with low coal porosity and metal iron content.

Wood char is known to have a considerable dependence on the layer charge and edge charge pH. Therefore, a decrease in the cation exchange capacity should be expected in parallel with the decrease in pH. Neutralization suppresses the oxidation of sludge and precipitation of chelates may improve the adsorption to wood char with high mesopore structure as seen in **Figure 8**.

As seen **Figure 9**, The bicarbonate hot waters affect the waste seepage in the copper mining leachate zone. The high level of iron and lead show the contamination at char load change, high level fly ash suspensions at 10% weight rate with 22% volume rate obtained microwave washing stepwise cycled- depending on the neutralization salt concentration added at 10 g-100 mg.

Figure 7.
The change in metal sorption depending on the metal concentration incorporated in the coal char/fly ash suspensions.

Figure 8.
The change in metal sorption depending on the metal concentration incorporated in the wood char/fly ash suspensions.

The high level of geothermal spa waters and heap leachate lead and cyanide metal complexes could be adsorbed by coal char and wood char suspensions by microwave act decantation unit, cycled washed and enhanced with use of hot waters. The outcome effluent of clarification treatment and injection to subground as shown in **Figure 10**, rehabilitate the irrigation area with the contamination at cyanide or metal load at high level even by means of fly ash suspensions at low weight rate, 10%.

4. Conclusions

This waste geothermal source combined with the discharge of inefficiently treated wastewater discharge into surface water sources. The method protect farming and irrigation sources imposed a direct threat not only to existing macro and microflora and fauna, but also to the provision of good quality water required for all socio-economic functions. For this reason, continuous monitoring of the operating status of geothermal wastewater treatment plants is increasing the importance of the environment and fresh water source become a key factor in determining the amount and quality of wastewater clarified and decanted by the relevant municipalities.

It is understood that public institutions and organizations have almost completely lost their functions in the field of gold heap leaching, mining waste production and the private sector has difficulties in finding financing and making

Figure 9.
The geothermal hot water of Güçlükonak in Şırnak changed neutralization and metal sorption depending on the metal concentration incorporated in the wood char/fly ash suspensions.

Figure 10.
The proposed feed flow into ground water, stability change in contaminated metal level, the sorption manner depending on the active site incorporated in the wood char/fly ash suspensions.

investments, necessary work should be done to create an alternative energy policy based on the country's domestic and renewable energy options, which are more environmentally sensitive. Waste materials of coal mining may promote the neutralization and fertile carbon healing of soil.

Since water in our country has scarce and hard environmentally undesirable chemical content, R&D studies that positively affect treatment efficiency in treatment model determination and cost for aim to minimize environmental problems should be focused on, these studies should be planned and encouraged by the government. License splitting practices, which have negative consequences in terms of production and efficiency, should be abandoned immediately in the evaluation of reservoirs in ground controlled basins.

Water management, ground water control, waste pool design, slime control and hydro power plant projects significantly need that; waste water management and ground waters should be analyzed in environmental, social and economic terms as a whole, and it should be decided whether the projects will be implemented considering the social benefit.

In reservoir basins, hydro power electricity generation activities, priority should be given to the people of the region in employment and the needs that arise during these activities should be met from the region as much as possible and focus on regional development.

In the use of fresh water, the current and advanced technologies in the world should be followed and the use of these technologies should be encouraged by legal regulations.

The waste water Law, the Environmental Impact Assessment Legislation, the legislation that has a direct or indirect connection with the electricity generation from hydro power plants, should be rearranged by a structure that includes professional associations, universities and non-governmental organizations with a steadfast understanding that takes into account the needs of the society.

The energy that society needs; It should be offered to the public with equal opportunities regardless of population density, water scarcity and region, and it should be ensured that energy, which is a human right, is cheap, reliable and accessible.

Heap leaching applications for gold and copper productions in the area is planned the feasibility reports regarding environmental contamination shows some degree of contamination and certain collection pools and seepage area will be highly contaminated by atmospherical dry conditions. That hard winter conditions oxidized the contaminating oxidation products in the ground water streams and dry weather conditions with scarcity of water may affect the cattle breeding and fish farming by evaporation of clean fresh water sources in the summer term.

In the pH measurements made, the pH value of 7,3 in washing hazardous waste water finally at the last washing column decreased to 5, depending on the concentration of salt content of sorbents in the water.

Stepped microwave heated washing test measurements showed that washed waste waters obtained after cycled at third steps in duration of 2 hours time in slow decantation flow using hot water with alkali bicarbonate and sulfite matter flow with 1 mm sorbent packages showed reductions in Pb, Hg and Fe at 37% performance.

In clean water aliquate had the 22 ppm Pb, 5 ppm Hg and 67 Fe chelate and precipitated Pb reduction at step model with nitrate is observed. The clean washed water is 0,73 ppm/min.l, Hg and total Fe reduction rate are decreased to 0,43 ppm/min.l and 0,23 ppm/min.l, respectively.

Abbreviations

Greek symbols

<i>a</i>	affinity parameter of the Langmuir isotherm (L mg^{-1})
<i>b</i>	stoichiometric constant defined by

B	reactant solid defined
Bi_m	Biot number for mass transfer
C_i	concentration of manganese in the bulk external phase of stage i (mg L^{-1})
C_0	feed concentration of manganese in the column (mg L^{-1})
D_{ef}	effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
F	objective function
h	fixed bed height (m)
k_e	mass transfer coefficient in the bulk external phase (m s^{-1})
k_r	reaction rate constant for heterogeneous systems (m s^{-1})
N	number of stages
Q	volumetric flowrate ($\text{m}^3 \text{s}^{-1}$)
q_i	concentration of immobilized manganese within the adsorbent particle at stage i (mg g^{-1})
q_m	theoretical maximum adsorption capacity of the Langmuir isotherm (mg g^{-1})
r	radial distance from the center of the particle, $0 < r < R_p(\text{m})$
R	radius of column (m)
R_p	radius of adsorbent particle (m)
R^2	determination coefficient (—)
$r_{c,i}$	unreacted core radius at stage i (m)
t	time (s)
V_i	volume of stage i (L)
α	backmixing coefficient (—)
φ	column hold-up (—)
ρ	density of adsorbent particle (g m^{-3})
τ	mean residence time of fluid in the column (s)

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