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Adsorption of Heavy Metals by Microwave Activated Shale/Asphaltite Char/Zeolite Granule Composts from Hazardous Sludges and Industrial Waste Slurries

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Abstract

There is a great concern about surface water pollution with high level mercury, lead (Pb) over 10 mg/l, 30 mg/l to the fishing lakes and streams in Şırnak Province even contaminating fresh water fishing and poisoning of human by mercury and lead in the region. The chromium over 50 mg/l from industrial seepages was disposed to lakes and streams in our country. There is a great green concern prompting land in order to control acidic mine waters so that the research study controlled and avoided hazardous metal limits of residual stream contaminants of heavy metals by sorption local clay and zeolite compost. The contamination rate changes to those based on seepage concentrations and wetness. The stream amendments, such as shale char carbonized from Şırnak asphaltite containing 52–60% shale activated by acid washing under microwave radiation as geo material composted for waste water treatment should control contaminated effluents concentration. The field studies to evaluate the stability of heavy metal concentrations and salts were scarce. The initial objective of this study was to determine the effects of seepage flow to surface and groundwater from the industrial discharge. In this study, important investigations have been made on composite granules production with Şırnak shale char and zeolite feed in order to activated in microwave oven 2 M HCl dissolution. The compost sorbent for high level heavy metal sorption in laboratory water packed bed column adsorption compost system. However, the results of filled packed bed zeolite yield high metal transfer to compost. Due to the complex chemistry of shale pores, and high porosity, heat conduction improved in the microwave sorption depended on granule size decreased. The other heavy metal sorption distribution was changed in the activation dependent on the microwave heating power.

Keywords: zeolite, 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, zeolite composts, shale

1. Introduction

This investigation of water treatment firstly proposed to control mud in acidic manner even dissolving hazardous coal mine cadmium, lead and mercury can be extremely hazardous in fresh water source contamination even industrial waste water management. The contamination research by soil remediation was existing in water logged areas. The strategical problems of water contamination and treatment by different type clay composts and the quality of them mostly exist in the irrigated areas like in South Eastern rocky plains of Şırnak and Batman, Turkey. The climate change and ground water changes generally resulted in over irrigation, seepage losses through channel and distributions, contaminated water control, management practices and inadequate control of drainage system. Analysis of high water table in water logged areas and drainage of irrigated areas have not been paid adequate attention in the planning and management of water resources, partly due to lack of requisite data and partly due to flood and rainfall in the country. In order to develop suitable water management strategies and controlling the extent of water logging in the area. GIS may facilitate the reconstruction of the ecological environment but also to accommodate the sustainable development of the water resources and waste water. In this study, the control of lakes and streams by hydrological characteristics of the Batman city were explained and the effect of soil characteristics on the the city was examined. In the investigation, hydrological features and the urbanization with new settlements need modeling regarding available water source. The hydrological property of settlement areas with dense populated areas in the model was determined by Geographic Information Systems (GIS) techniques. The main purpose of this study is to investigate the effect of settlement on the basic hydrological structure by studying the characteristics of the ground topography, ground water elevation, slope and viewing. GIS techniques were used in the creation of the thematic maps and in the analysis of the parameters. Finally, the GIS study models created, the available water source change and a stream contamination model was provided sufficient source control at the Batman province. The presence of this stream and lake contamination, soil structure in the Batman province reveals the contamination by acidic mine waters and potential flood scale and flood risk. This study produced more hazardous contamination data with hydrological streams discharged to lakes and streams with GIS. GIS has made it possible to obtain more qualified data by enabling the use of waste water treatment by mobil units in this research (**Figure 1a and b**) [1, 2].

The hydrological studies carried out by Water Association showed that high level Tigris river stream flows from 650 m level attitude through 610 m–600 m levels laguuns in Batman province with hig risk of flood (**Figure 2**).

The chalky limestone layers of Batman province reveals high amount of water suddenly at the stream below levels to 2 m high over agricultural wheat land and the potential flood risk line [2] (**Figure 3**) [1–3].

1.1 Accumulation of contaminating acidic waters, heavy metals and distribution in floods and laguuns near dams

The oxygen content and and electroopotential of waters adequately accounted in stream flows causing animal feed contamination n the pastoral fields by soil and growing grass near by this contaminated stream laguuns.

In the hot streams and acidic mine waters the ferric iron and sulfate tend to be highly common as AMD seepage, alkali resulting from the reduction of these two species, a weak base (bicarbonate) and producing astrong base (hydroxyl ions), also generate net alkalinity (Eq. (8)). The indirect acid production was relatively high

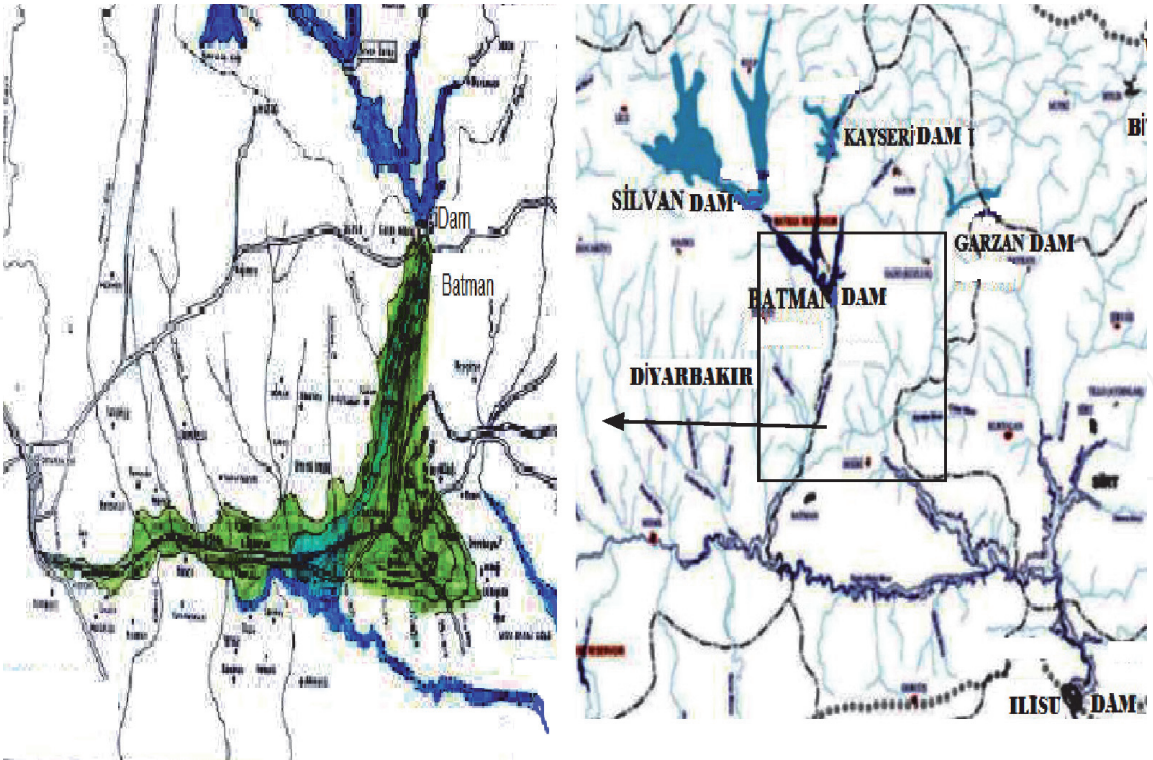


Figure 1.
(a) Groundwater Flows and Hydrological Stream Discharges in Batman Province at scale of 1/20000
(b) 1/50000.

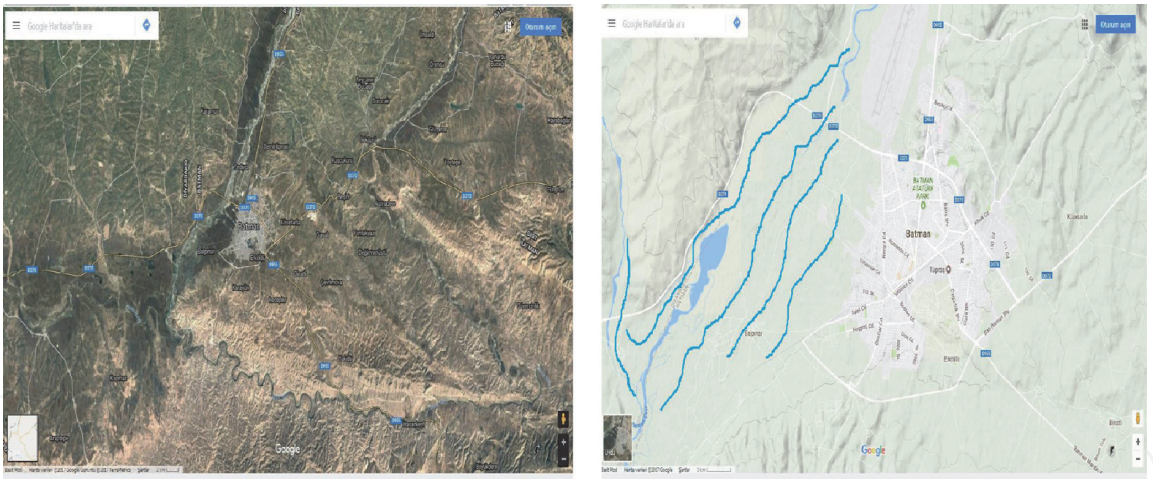
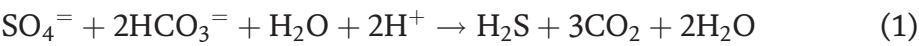


Figure 2.
(a) Satellite view of Batman City and province reveals the potential flood scale 1/20000 and (b) earth view with flood risk water lines of Batman City and province 1/20000.

rate at higher pH levels over 5 with dissolution of heavy metals in sulphide minerals and neutralization by alkali matters govern the dissolution by the reactions as given below [4–6];

Bicarbonate sulphate hot streams reduce acidity as below Eq. (1).



The sulfide produced is strongly reactive towards heavy metals as given Eqs. (2) and (3):

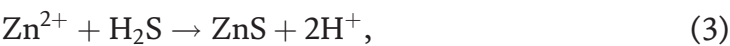
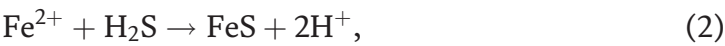


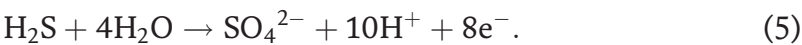


Figure 3.
Batman province some set reveals the potential flood ban and flood risk.

which form very insoluble sulfide compounds. FeS is unstable relative to pyrite and the further reaction, which is an oxidation of S^{2-} to S^- , as given in Eq. (4);



generated in the late muds close to the settled mud - water interface. ZnS and PbS, in the sulphide complex structure are much stable and retain S in the -2 state. However, the sulfate part of reaction Eq. (5) [7, 8] may cause redox effect an oxidation. Then.



The aerated and oxygen rich waters oxidizing sulphidic character metal precipitates to sulphate and chloride dissolution by unstable forms, but over pH 9 as shown in Figure electropotential matter of waste waters provides hydroxide precipitates in soil mud. Even jarosite form precipitates occuuring in hot water streams area with redish brownish precipitates, however those type residuals stuck over sand may become sweet salty alg fish feed even causing 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 potential contamination [7–13] of fresh waters soueces at pH Eh diagram stability as given in **Figure 4a** and **b** folowing flood.

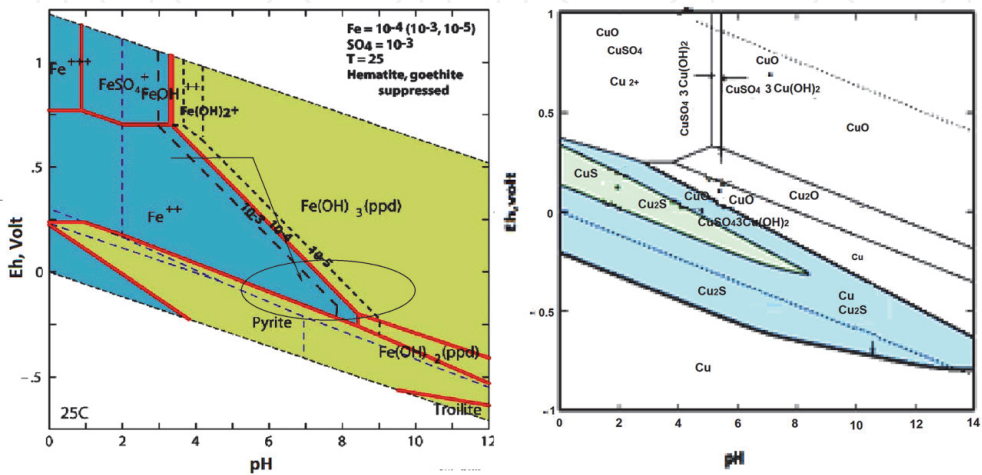


Figure 4.
(a) Eh-pH diagrams for metal Fe and (b) Eh-pH diagrams for metal Cu stability.

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

$$\frac{dc_{Pb}}{dt} = k_i e^{-t/c} \quad (6)$$

Where c_{Pb} Lead contamination mg/l, k the rate of dissolution of lead, i is the reaction style, t is time,

The dissolution concentration of accumulated metal in aliquate of lake streams as regarding Pb heavy metal contamination is followed by equation, where n is kinetic order type

$$\frac{dc_{Pb}}{dt} = k_i c^{tin} \quad (7)$$

The dissolution concentration of accumulated metal in aliquate of sulfurous hot water streams as regarding Pb heavy metal contamination is followed by equation, where SO_4^{-2} sulphate concentration in effluent. f_i is concentration rate of sulphate

$$\frac{dc_{Pb}}{dt} = k_i c^{tin} . dc . f_i (SO_4^{-2})^{tin} \quad (8)$$

The dissolution concentration of accumulated metal in aliquate of limestone rocks dissolution by hot water streams in subground lakes with high CO_2 gas dissolved streams as regarding Pb heavy metal contamination is followed by equation, where HCO_3^{-2} bicarbonate concentration in effluent

$$\frac{dc_{Pb}}{dt} = k_i c^{tin} . dc . f_i (HCO_3^{-2})^{tin} \quad (9)$$

The dissolution concentration of accumulated metal in aliquate of high fertilizer dissolution by wrong amount of fertilizer use in the agricultural fields discharged to streams as regarding Pb heavy metal contamination is followed by equation, where HNO_3^{-2} nitrate concentration in effluent

$$\frac{dc_{Pb}}{dt} = k_i c^{tin} . dc . f_i (HNO_3^{-2})^{tin} \quad (10)$$

The dissolution rates of heavy metals in acidic mine waters and sulfurous hot streams occurred in the region of Ilisu Dam, Güçlükonak, Şırnak and Batman Province sites. Fish farming require below 1 mg/l Pb Cu and Cd and Zn in which basaltic rocks and copper ore deposits contained highly around %1-2Pb and 200 mgCu at high attitude deposits in Siirt and Şırnak. The contamination of some accumulated heavy metal contents of hot streams and soils in the region are given in **Table 1**.

Urbanization and economic growth in the high populated Batman city evolved along with the management of natural resources. In this process, provision of drinking water supply and distribution service for urban areas also developed on the same plane. The effective role of the public was felt in meeting the water resources management and service. Infrastructure investments are centrally located, water resources are found, structured, stored, distributed and refined. Large investments have been made in order to meet the fresh water need. The use of water resources (water withdrawal and level shift) and evaluation for development and community needs have been studied. However, the amount and quality of water that the

Effluent, mg/l	Şırnak coal mine pool	Şırnak, hezil stream	Güçlükonak hot stream	Batman hot stream	Şırnak kasrik laguun	Ilisu dam laguun1	Ilisu 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 1.
Şırnak and Batman province reveals the potential contamination scale and high contamination risk of fresh water source with flood.

ecology need is not addressed. Everything is built on the theme of “develop-supply-use”. Parameters considered in the planning of water resources were population estimate, per capita water demand, fish farming, agricultural production, economic productivity level.

1.2 Fish farming in water lakes and streams

The hazardous high level contaminants occurred in the such acidic seepages or acidified chelate mixing to streams should be neutralized by oxidizing reagents such as ozone or neutralizing alkaline washing so that resulted effluent contamination by Hg, Pb, Cr, Cd, Cu, Zn, Fe, SO₄ rates were so low. The oxidation recycling of residual contaminants was not a serious threat using these parameters, future water demand forecasts are used and these estimated values are used when designing the systems to meet the demand. In this approach, the demand for water has been determined independently of the specific needs of fish farming, agricultural irrigation, and human needs, the amount of water a healthy ecosystem will need, or actual regional water availability. The next step in traditional planning is to identify projects that will reduce the gap between estimated water supply and demand. In every scale, the planning action (region, basin, city) is used for the regular and healthy spatial development uses (housing, commerce, industry, recreation, other

social) in the metropolitan cities which are especially migrating in our country and in medium size settlements. Such as equipment as directed by location decisions; It also determines the water demand of the city at the same time with its population and density of buildings and its quality and quantity of usage. While city plans shape the socio-economic and physical structure of the city, with the proposed land use, employment, population and density decisions, the city's daily water demand is also shaped. Therefore, any kind of urban development outside the plan creates an unhealthy environment that affects the quality of life of the city, as well as poses a serious threat to the water resources (increased water consumption pressure and pollution) (Urban Planning Chamber Water Commission, 2006). Survey, planning (feasibility) and Project work will be given efficiency. The quality of the water quality will be preserved, improved and monitored. Heavy metal contamination hazard maps will be prepared and an early warning system will be established.

Nowadays, oil, grease and other pollutants as absorbent material in cleaned, bleach mud in food industry, in pharmacy adsorbant, as a catalyst carrier in the chemical industry and in many other industries it is used for various purposes. Clay bentonite, which is used as industrial absorbant, sepiolite, atapulgite and kaoline. This clay is good absorbant or active bentonite or montmorillonite. it is highly demand for absorbant substrate for fresh fruit drinks and brewery, water treatments in Europe. The consumption has increased to around 5 million tonnes/year in the 2020s while in 1994 it exceeded 2 million tons/year. In terms of bentonite and sepiolite, it is known that it has large beds and it is enough on these beds until recently research work was carried out for heavy metal contamination. In this study, bentonite and other clays, shale and marly shale of Şırnak and absorbance properties, areas of use, production and market conditions. The bulk density of absorbant clay bentonite and atapulgite, the amount of moisture and the absorbant capacity. Bentonite and atapulgite absorbance by passing through certain processes was performed and the absorbance was measured at the mechanical strength change has been studied.

In general, a grainy and fine grained the raw materials described as the shale, kaoline, illite, marly chlorite and smectite alteration coverings of rich rock abrasion and carry over fresh water occurs in the basins. Kaolinite, montmorillonite, illite, chlorite, sepiolite and atapulgite or several quartz, cristobalite, amphibole, feldspar, calcite, magnesite, dolomite, gypsum, alunite, and natural clay containing one or more minerals heterogeneous mixtures [7]. Mineral depending on their content and chemical composition. As the color of the killer, white, pink, gray, green, in various shades of yellow, blue and brown [8]. The chemical analyzes indicate that the killer is mainly silica, alumina and water can be distinguished in most cases iron, alkali and alkaline earth in quantities. In this study, montmorillonite group bentonite and chain clay atapulgite used.

DTA curve and the water away from the cation between the layers. In addition, endothermic DTA peaks originating from the removal of H-bound shale in the samples were observed at approximately 200°C, and endothermic peaks of hydrate bound to the Brønsted centers were observed at approximately 300°C.

The fact that clay and clay minerals, which constitute a significant part of the ground and underground resources of our country, are not processed sufficiently is an important issue that causes serious economic losses for our country. In order to produce clay minerals in high quality and desired properties, some processes such as acid activation, organo-clay preparation, microwave dissolution, calcination and cation exchange are used [12–15]. Acid-activated clay, known as bleaching earth, is used in scientific research as a selective retainer, catalyst, catalyst support and in the differentiation of the killer [16]. Bentonite with desired surface properties, porosity and hence retention capacity is mainly produced by dry or wet acid activation using

mineral acids such as H_2SO_4 and HCl [17]. The main purpose in acid activation is to reach the desired structure without disrupting the layered crystal structure of the clay. For this reason, the acid/clay ratio, temperature, acidity, acid concentration, type and duration of activation, kiln type and physical properties and amount of washing water are important considerations to be taken into account when performing the appropriate activation.

1.3 Zeolite - clay compost with brønsted and lewis acid centers

The Brønsted acid centers are mainly associated with the inner layer zone and the Lewis acid centers with clay marginal surfaces. The water molecules in the spheres surrounding the exchangeable cations are protonic depending on the degree of polarization of the metal cation and behave as Brønsted acid. In addition, the surface silanol groups (Si-OH) resulting from the breakage of the Si-O-Si bonds in the tetrahedral layer in the killer contribute to the Brønsted acid centers. Lewis acid centers are also associated with the co-shaped exchange of the Al^{3+} and Mg^{2+} cations in the octahedral layer and the Si^{4+} and Al^{3+} and Fe^{3+} cations in the tetrahedral layer, albeit associated (Figure 5) [18] with metal atoms on the crystal edges. The oxygen planes in the space between the plates act as a pair of electrons, ie Lewis bases. The Hammett acid indicator technique, the n-butyl amine back titration technique and the investigation of the attachment geometry of the species such as cyclohexylamine, n-butylamine and pyridine can be used to determine the species and amount of acid centers in clay minerals rapidly [18, 19].

The increasing demand of bentonite utilization for advanced material technology and the limited reserves of high quality bentonites push the reserachers and the operators/producers to evaluate the lower quality calcium and mixed bentonites for the replacement of Na-bentonites in use. The technological properties of bentonites, however, can be upgraded by the application of concentrating and alkali activation. Mostly, wet concentration methods such as decantation, hyrocycloning and centrifuging have been applying and water quality and ion type/amount which the water carries becomes more important to controll the further activation process

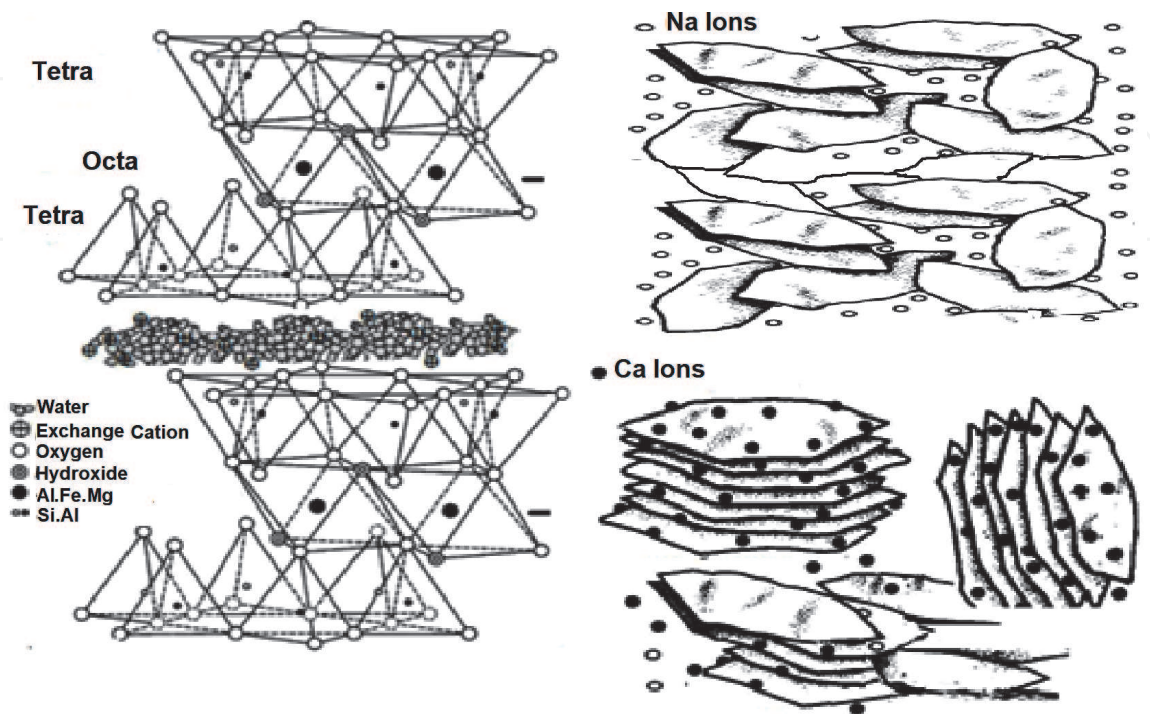


Figure 5.
Clay structure welling manner prompts adsorption of heavy metals.

since bentonites carry the releasable and exchangeable cations on interlayers which interact with ions in water.

In this study, the effect of water quality (ion type and amount in water) was subjected to the concentration and further alkali activation tests with mixed type bentonite received from Resadiye/Tokat bentonite deposit. Deionized, filtered and tap water and syntetic water including different salts namely $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , MgCl_2 , KCl , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were used as separation media in concentration by settling and decantation. The effect of water quality on concentration and alkali activation were declared based on the pH, CEC (Cation exchange capacity), viscosity, swelling index and filtration loss.

Bentonite, the commercial name of montmorillonite from the clay minerals of the smectite group, shows colloidal properties when mixed with water, and its properties such as water swelling, high plasticity and ion exchange capacity are due to the three-layered crystal structure [21–28].

2. Sorption matter

The large surface used for industrial purposes natural materials [7]. Absorbents and adsorbents generally used bentonite; Simectite, Atapulgit, Sepiolite. It can be classified as montmorillonite. The smectite group is one of clay minerals or kill more with more or less called bentonite. Bentonite base mineral montmorillonite is common for the killer and is a commercially used term, at least soft, containing 85% montmorillonite, is an aluminum hydrosilicate with a colloidal property. When mixed with water, density of a few solid swelling bentonite about 2.5 g/cm^3 . montmorillonite is calcium in many countries. Bentonite is a given name and the main content which is montmorillonite and can change mainly cation can be defined as clay with Ca; Atapulgit, $2\text{MgSi}_8\text{O}_{20}(\text{H}_2\text{O})_4$. The palygorskite expressed by the formula $4\text{H}_2\text{O}$ an aqueous magnesium, aluminum silicate. Sepiolite is $6\text{Mg} \cdot 9\text{Si} \cdot 12\text{O} \cdot 30(\text{OH}) \cdot 4 \cdot 6\text{H}_2\text{O}$ group is aqueous Mg silicate. In these minerals channel-shaped pores water bound to crystal structure with molecules. The clay in this group is micropore and channels and large surface area due to the possession of various substances absorbers and adsorbing capacities It is high.

2.1 Absorbent of bentonite and shale/clay features-waste water soil absorbent

Clay minerals in various industrial processes use, compositions and compositions are closely related. Grain size, grain shape, surface chemistry, surface ceramics, color, etching, viscosity, plasticity, absorption, adsorption v.b properties of clay minerals significantly impact on the use of. Absorption can be carried out in the presence of water or other liquid. Absorbents material is water and other liquids is a sponge as material containing zeolite and shale pores and the pores of the mass (solid material) such as shown in **Figures 6** and **7**.

The main use of clay as an absorbent areas, ground absorbtion and cat litter, is the carrier of the drug. The high absorption capacity, the material large surface area, large pore volume, with sufficient pore size and distribution caused in developed matter of mass transfer and diffusion. In addition, its mechanical strength must increase when it gets wet. Bentonite, known as an absorbent clay, shale, sepiolite and atapulgit features have a large size absorbent material. Bentonite clay absorbance capacity, porosity, specific surface area, specific pore volume, and the pore size distribution of the acid, base and salt as well as chemical processes such as can also be increased by heat treatment [11–14]. Different absorption depending on clay type processes, for example, montmorillonite to the outer surface of the swollen hair water between the inner layers causing swelling which sorp waste water

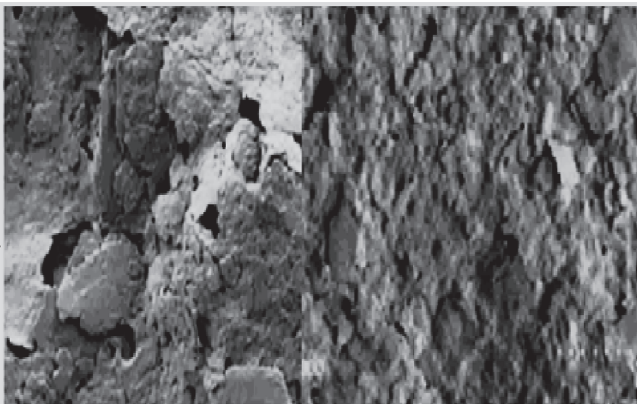


Figure 6.
The composite sorbent use, zeolite distribution in pellet.

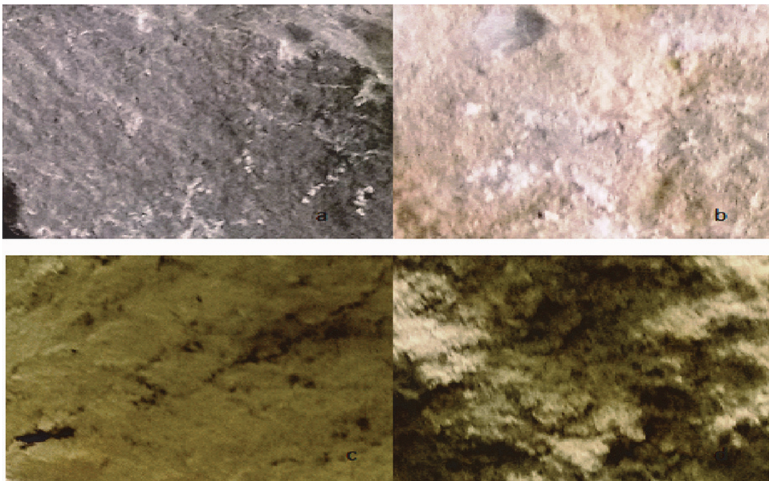


Figure 7.
The micro pictures Şırnak marly shale char shale as sorbent.

contamination. Sepiolite and atapulgite water absorption in a chain structure outer surfaces and zeolitic channels. In this type of structure of caged crystals there are no swelling between. The feature of the absorptive fluid is that the clay granules affect the absorption capacity. Liquid density, viscosity and surface capillary absorption of tensile clay granules are important factors affecting.

The absorbant clay bentonite was sorptive, colloidal, catalytic and rheological properties as given in **Table 2** [15]. Work in industrial waste watercleaning areas, non-burning, slippery to create a safe working environment absorbant killer is used [16–18, 28]. In the amount of clay used for hazardous waste water treatment increased over more than 180,000 tons/year.

2.2 Zeolite/asphaltite shale char composite

This area is especially montmorillonite, bentonite type clay used waste water treatmment. The floor of the bentonite granules use as absorbant in 2020s started, but until the 2nd world war did not show improvement. The industrial waste

Unye bentonite	800–980 kg/cm ³
Sepiolite	400–700
Zolite	700

Table 2.
Shale and Marly shale bentonite properties.

waters: soma factory, airplane hangars, ship buildingbenches, other production facilities andIn the workshops, grease, oil, water, chemicals and other undesirable substances absorbed and cleaned.

Zeoite as filler material is commonly used as cat litter, granule powder do not build up, do not spread bad smell, granule grain size, basic as absorption capacity by the cat should be accepted. High absorption capacity having clay, only to absorb the urea not ventilated, but bad reduce smell and bacteria should avoid. The grain size distribution of clay granules it is important that it is usually between 1 and 6 mm is required. The beads are in the cat's claws. and its flanks and rounded surfaces should be. Cat litter, transport and use so as not to create dust during must have mechanical stamina [21].

2.3 Microwave treated briqutting of biomass char/zeolite composite

Washing of hazardous waste waters by microwave action efficiencies exceeding the total Fe Pb and Hg contents of sludges increased fast on coal char and wood char were also reported by Tosun [13].

2.3.1 Physical surface properties of char

BET specific surface areas, total surface activity, oxygen functional groups, total surface impurities, metal concentrations, dielectric value, free radical concentration and reactivity were related to the stimulation of oxidation reactivity. However, in some investigations, the pore size distribution of activated carbon is alsa likely to affect desorption kinetics [22–26].

3. Material and methods

3.1 Zeolite/carbon compost washing technology - sorbent applications

The chemical compositions of used local rock materials in waste sludge treatment (**Table 3**) [23].

During the experimental studies bentonite and zeolite samples, Ünye region, was investigated with intermediate type bentonite; pure, purified, tap water and

% Sorbent	Şırnak limestone	Simak marly shalestone	Şırnak marl	Şırnak claystone	Expanded clay/zeolite
SiO ₂	3,53	9.42	24,14	48,53	48,53
Al2O3	2,23	6,53	12,61	24,61	24,61
Fe2O3	0,59	4.48	7,34	7,59	7,59
CaO	49,48	39,23	29,18	9.48	9,48
MgO	2,20	2,28	4,68	3,28	9,28
K ₂ O	0,41	0,53	3,32	2,51	2,51
Na ₂ O	0,35	0,24	1,11	0,35	0,35
Ignition Loss	46,19	26,11	21.43	6,09	0,09
S03	0,32	0,21	0,20	0,32	

Table 3.
The chemical analvsis values of limestone, marly shale stone and clavstone of Şırnak province.

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , MgCl_2 , KCl , AlCl_3 at concentrations ranging from 31,125 to 1000 ppm. Bentonite suspensions prepared by adding synthetic waters such as $6\text{H}_2\text{O}$ and bentonite suspensions were decanted by sedimentation method for 30 minutes in a 2 lt scale and bentonite concentrates were obtained and then necessary test and characterization procedures were applied afterwards.

Decantation was carried out in 2000 ml mills by adding 75 gr bentonite to 1900 ml of water. For a homogeneous suspension mortar, the bentonite water mixture was first subjected to scrub treatment in a Denver flotation cell for 5 minutes.

After the scrubbing, the suspension was allowed to stand for 30 minutes after being agitated so that the impurities were precipitated. At the end of the period, suspended bentonite concentrate was removed by titration method and then was dried.

The same procedure was repeated with synthetic waters prepared by adding salts at concentrations ranging from 31,125 ppm to 1000 ppm, until the bentonite concentrates were obtained in sufficient quantities with pure water, tap water and purified water.

The layout of the washing cycle is somewhat simpler than that of the lime slurry: there was no water–compost washing column towers connected to the waste sludge, and the washing unit contained one single microwave radiation column can be used to perform the three decantation washing phases: roughing, scraping and cleaning. The variation of the third cycle washing was also more limited recycled 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 and amounts (of at least 20°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.

4. Results and discussions

4.1 Langmuir absorption model

For an overview of these more innovative and prospective applications, the general common method can be given in **Tables 4** and **5**.

The first order sorption concentration at three stage cycling counted by the equation below:

$$\ln c^{pb} = 1 + \frac{k_1 t}{1!} + \frac{k_1 t^2}{2!} + \frac{k_1 t^3}{3!}, 3\text{ppm} < x < 300\text{ppm} \quad (11)$$

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 4.
The activated bentonite compostwith 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 5.
The activated zeolite compost with char shale of Şırnak materials.

It has been found that the amounts of CaO and Na2O decrease due to the replacement of the Na⁺ and Ca⁺ releasable cations between the inde layers with the H⁺ ions. Mg and Fe atoms in the octahedral crystal grains and the Al atoms in the octahedral centers, as well as the Al atoms in the tetrahedral layer, as well as Al2O3, MgO and Fe2O3. Make octahedral after bentonite from X-rays data elemental analysis data suggests that even lower coordination Al atoms are present in bentonite and less in the activated clay. The activated bentonite suspensions captured high level heavy metals such as Pb and Hg in the sludge (**Figure 8**).

Samples for this heat treated at different temperatures certain properties of the zeolite material (high absorbance capacity and not dispersed in the wet state) possibility of research and results as given in **Figure 9**.

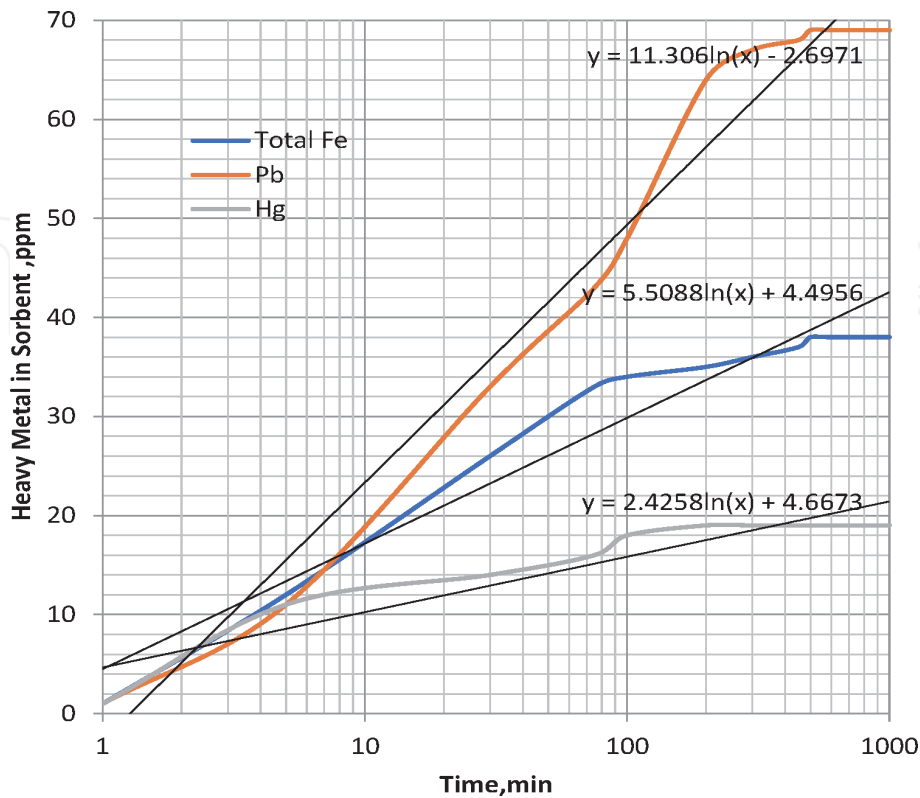


Figure 8.
The change in metal sorption depending on the metal concentration incorporated in the bentonite suspensions.

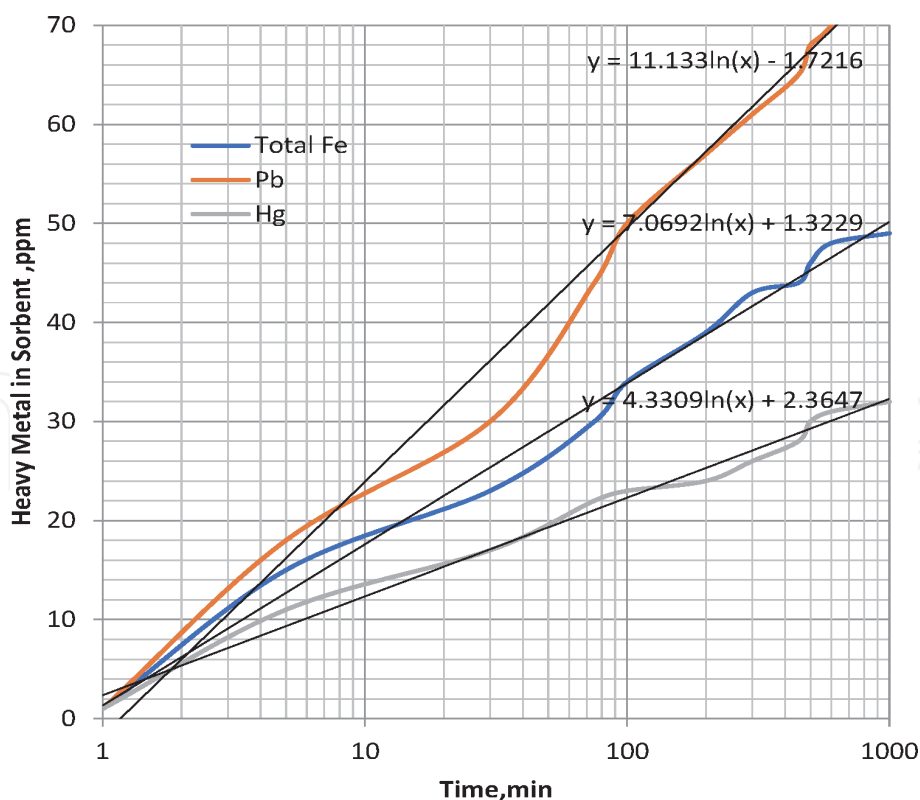


Figure 9.

The change in metal sorption depending on the metal concentration incorporated in the zeolite suspensions.

Cation exchange ability was so effective in metal sorption manner. The pH was efficient criteria in the washin column sorption.

It can be seen in the above graph, the pH decreases inversely proportional to the amount of salt added to bentonite suspension, which is much more noticeable when FeCl_3 is used.

Bentonite 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.

The FeCl_3 20 mg added bentonite solutions showed the change in cation exchange capacity (CEC, milliequivalent gram/100 gr) found in the bentonite concentrates and suspensions obtained using the precipitation-siphoning technique, depending on the salt concentration added.

4.2 Activation by HCl washing following methanol decay treatment under microwave radiation

The bentonite sample used in the study was obtained from Unye Madencilik from the Unye region of Tavkutlu mine. The bentonite sample was sieved and a small part of 45 μm was used for the operation. Bentonite samples were activated with 1 and 2 M HCl solutions for 2 h at 90° C using the Batch method (using 100 ml acid solution for 5 g sample). The acid-treated samples were washed with hot deionized water to remove Cl-ions and dried in room condition.

The microwave activated bentonite used in the experimental work was provided from the district of Unye in Ordu province. For the first time, Ünye region bentonite 0.1 M 100 ml CaCl_2 solutions were mixed in the beaker at room temperature for 24 hours and the filtrate was converted to the ion-exchange by applying the AgNO_3 test. Acid/clay suspensions were then prepared with bentonite, which was made to be ionized, to give H_2SO_4 /clay ratios of 2 M, These were named -bentonite. These suspensions were dried at 150 oC for 3.5 hours. 50 ml of distilled water was added to

the hot dry samples. The filtrate was filtered and dried at 80°C. Finally, 5 ml of chlorite was added to the acid activated bentonite samples, each of which was 0.01 g, and the shale was retained by exposure to methanol vapor at 60° C for 4 hours. In addition, these samples were further dried at the same temperature for 1 hour to remove weak chlorite species [22]. X-ray powder diffraction patterns of amorphous and acid activated bentonite samples were $\lambda = 1.54050 \text{ \AA}$ wavelength Cu K α /40 kV/40 mA RIGAKU 2200 diffractometer. Elemental analysis of the samples was performed using the ZSX 100e wavelength-separated X-ray fluorescence spectrometer (WDXRF) system with the Rigaku brand Rh anodic x-ray tube and the Rigaku SQX software package program. The specimens were stimulated with Rh anodic x-ray tube at 50 kV and 50 mA in order to reduce the damage that could occur in the samples during the measurement. PRIS Diamond brand TG/DTA thermal analyzer was used to obtain the thermal analysis curves of bentonite samples attached to pyridine. The thermal analysis curves of the samples were placed at a heating rate of 10°C/min, 5–10 mg of sample was placed in Pt crucible and taken against $\alpha\text{-Al}_2\text{O}_3$ reference sintered at 20–700°C in air atmosphere. Again ATR spectra of the chlorite-bentonite samples were recorded in the absence of disc preparation with KBr under vacuum at a Bruker Vertex 80 V spectrometer at 1700–1350 cm^{-1} . The surface areas of raw, activated and shale clay samples were measured with a Quanta Chromosorb surface analyzer. The surface area was determined by measuring the thermal conductivity using a gas mixture prepared in 30% N₂ and 70% He composition and taking into account the BET equation.

Thermal Properties were determined PRIS Diamond brand TG/DTA thermal analyzer. Thermogravimetric (TG) and Differential Thermal (DTA) analyzes of the samples used in the experimentation were carried out for dehydration and activation ability in sorption as seen in **Figures 10** and **11**.

4.3 Sorbent preparation for heavy metal absorption

The absorbance capacity of the microwave heated shale samples according to output zeolite, char shale and Ca-Bentonite experiments, the absorbance capacities were high, but high clay samples in water muddy have efficiently sorped Fe cations much. The results show that Na-Bentonite for this purpose seems unsuitable; from Breakup heat at high temperatures it must be processed but this the temperature of the absorbance has been detected. For this purpose the best result is about 400°C for Ca-Bentonite; the result is obtained at 200°C.

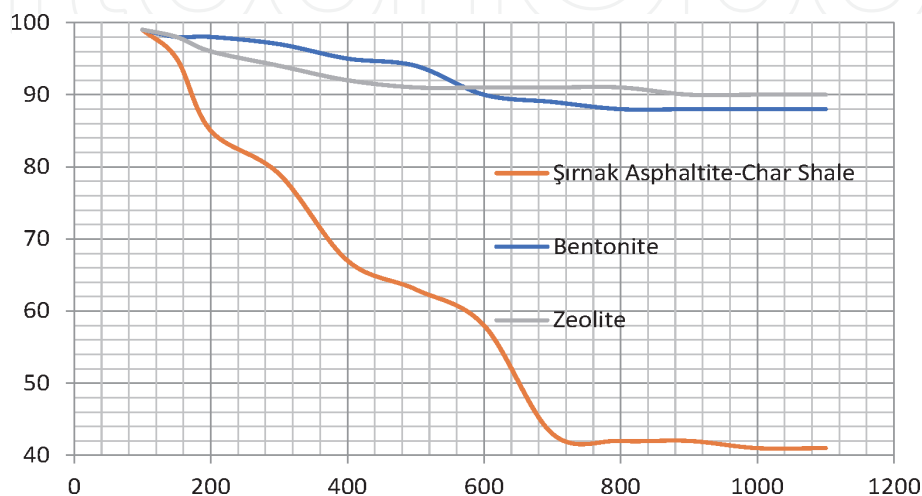


Figure 10.
TGA analyzes of the samples were carried out for dehydration and activation ability in sorption.

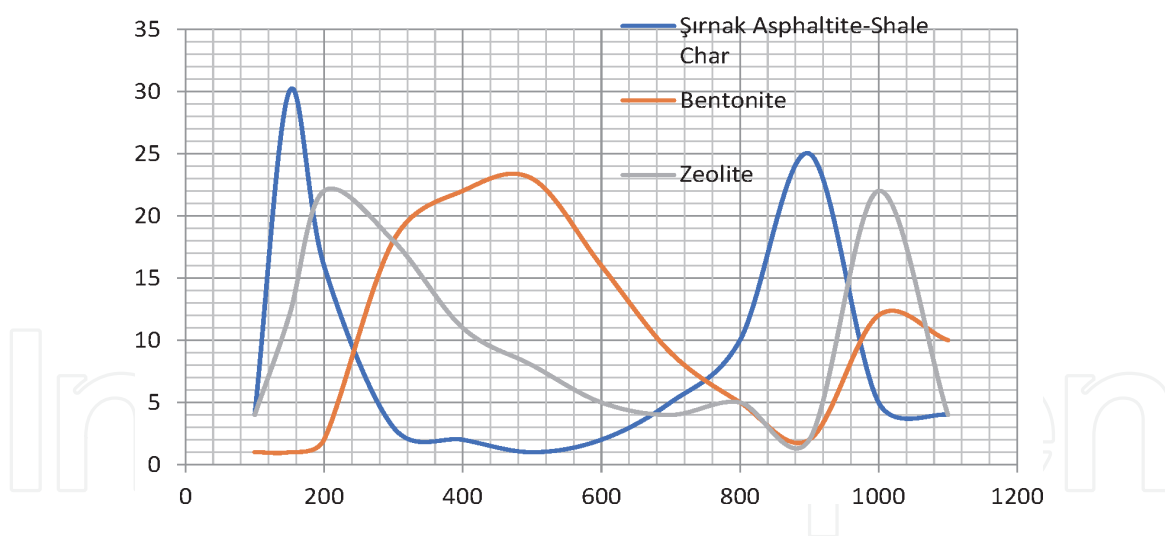


Figure 11.

DT analyses of the samples were carried out for dehydration and activation ability in sorption.

The current use of absorbent clay and new areas of use increase in demand due to outflow. Especially absorbent clay market, the cat and cat market A significant improvement in America It was. For absorbent clay deposits our wealthy country, too, to have a significant share of there is no reason why. This absorbent is limited to meet clay consumption. The number of welding to, Turkey clays alternative can create resources. For this purpose, existing in Turkey absorbant clay beds must be fully identified, potential sources should be determined, absorbant purposefulness should be investigated and suitable properties absorbent clay production. Detailed studies to improve processesIt should be done. This study result, Turkey absorbanceon the samples taken from the By applying the processes, Afnor standardssuitable industrial absorbant clay productionIt was possible. Turkey's evaluating the existing potential to take part in this market, the country economywill provide significant benefits in terms of Compliance with environmental norms.

4.4 Compost of zeolite/shale/carbon pellets for heavy metal controls in waste waters

Bentonite is one of the clay minerals containing montmorillonite. Structurally, montmorillonite has a 2:1 layer of alumina octahedral (O) layer between two silica tetrahedral (T) layers [18]. The negatively charged excess coming from the isomorphous shifts is compensated by the interchangeable cations in the layers [18, 19, 28].

The acid activation process is widely used to improve the adsorption and catalytic properties of natural bentonites. The impurities, such as calcite and dolomite, are removed from the structure by the treatment of montmorillonite with inorganic acids, the interchangeable cations are replaced by hydrogen ions, and some of the Al ions in the tetrahedral layer dissolve certain cations of Fe, Al and Mg in the octahedral layer [19].

As a result, acid activation increases the pore diameters of the bentonite surface and the surface area and adsorption capacity up to a certain amount of this application [20]. If the amount of acid used during the acid activation process is excessively high, the Al ions found in the octahedral layer dissolve more and as a result, the mineral structure collapses, leaving a skeleton structure composed of silica solids. This reduces the adsorption capacity of the clay and disrupts its selectivity.

Pb is a colorless and Hg. The main sources are fossil fuels such as Pb, acidic mine waters and toxic metal sludges, which are industrial plants and industrial steel washings. [21] during the metal smelting processes and other industrial processes.

Pb compounds, one of the most common Hg pollutants, combine with water droplets within sulfuric acid aliquates or acid rain. Acidic mine waters such as acidic rainfalls affect the chemical structure and biological conditions of the lakes and soil [22]. In addition, Pb Hg emissions are extremely harmful to health and directly affect the eyes, throat and respiratory tract [23].

Although the changes in the structural properties of bentonites after acid activation have been studied extensively in the literature, the studies on Pb adsorption of these samples are rather limited [24]. For this reason, the aim of this study is to investigate the thermal Pb and Hg washed adsorption properties of bentonites after acid modification and microwave activation.

The compost clays has substantial oxidation resistance and forming way service. This zero-pressure fluid provides precise, uniform temperature control to 500°C in closed-loop microwave systems where the heat transfer fluid is more than occasionally exposed to air. The fluid is comprised of a unique high-stability base plus high-performance oxidation inhibitor/stabilizer.

4.5 Carbon surface activation

In the sorbent size distribution, 80% of weights of samples were under 3 mm. The lignite samples were mainly distributed between 1 mm and 3 mm size fractions. The effect of particle size of solid sorbents were investigated over the combustion of Şırnak Asphaltite char shale and bentonite carried out well on acidic mine water of copper mine in Siirt substance subjected to reaction with bentonite clay in sorption, as shown in **Figure 12**.

Although metal diffusion on sorbent from waste sludge was believed to be the primary mass transport process in the absorption chamber, complex reactions proliferated the alkali clusters below 1-2 mm size and exothermic oxidation reactions increased toxic substances in the effluent form, a relatively porous structure of bentonite clay interstitial spaces and cracks reduced below 1 mm size. The hazardous heavy metal concentrations reacted adsorbate then adsorbs to the sorbent in an certain amount that is equal to the amount of previous adsorbate that was partially degraded on the surface of the bentonite clay and stuck covered toxins, along with avoiding chelating organic matter related carbonil and amine.

4.6 Washing sorption by clay compost control

The waste water washing provide the main support to the clean water production. The commercial successes in clay mud mentioned in washed bed and its

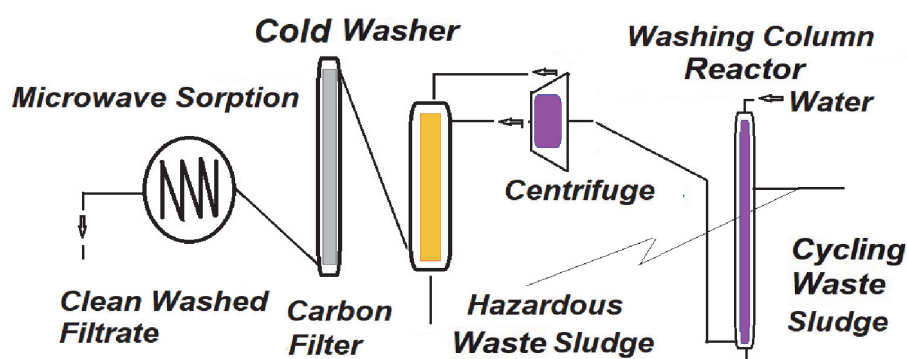


Figure 12.
Schematic view of an washing with microwave recycled by microwave sorption technique.

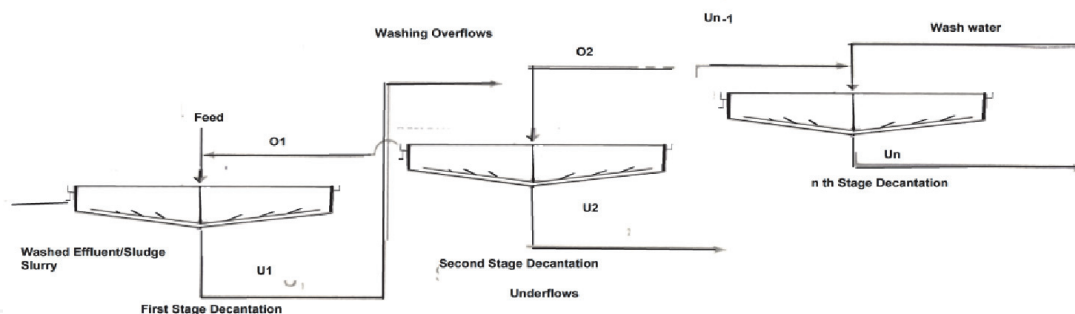


Figure 13.

The washing decantation by sorbent use, leaching in microwave activation as sorbent compost.

sedimentation ability were described some of the emerging applications in lime use like clean water neutralization, aeration [26]. The figures of statistical potential of washing control with different techniques in waste water cleaning are classified as seen in **Figure 13** regarding cycling decantation time.

Some cost evaluations covering security of supply and environmental impacts, climate change evaluations, and technical and economic analysis, may be discussed in cycling cost and activities [29–32].

Initially, most of the toxin removal occurs through chemical adsorption of the toxins to the expanded clay where the combustion temperature was in the combustion phase below 750°C that lasts approximately 2–3 mins. The removal efficiency of 40–90% were reported during this temperature range. Total organic toxin substances were completely slightly at efficiencies of 75–90% in the late combustion phase. The pictures of zeolite fines soaked in char shale/clay were illustrated in **Figures 9** and **10**. Following the combustion at 800°C adsorbed film of emissions over expanded clay was shown in **Figure 13**.

A common industrial combustion to control the emissions pre combustion stage lime washing involves backwashing with air and hydrated lime water rinse. Process variables include the control backwash rate, surface wash rate/duration, time sequence and duration of backwash. Clean filtrate is pumped back into the bottom of the column during backwashing.

5. Waste water treatment

The required test and characterization procedures such as pH viscosity measurement, filtration loss and swelling index were applied to all bentonite concentrates obtained and then to products activated with 0.5% soda.

These sorbents need to be accurately mixed with combustion matter and to optimize the combustion process. Reliable models, based on the above results, need to be combustion chamber construction for the estimation of kinetic parameters for toxic stream control. Such toxic stream circulation models would aid in the microwave activated shale clay sorbent use in waste water treatment systems as shown in **Figure 8**.

The country needs the cleanest fuel to be produced providing the essential oils and gases. For this reason, acidic mine waters as heavy metal contamination to control fish farming were mixed with expanded clay at 1–2 mm size soaked with slurries of different alkali sorbents such as bentonite, shale fine, NaCl, CaCl₂ and KCl were tested in the packed bed column washing and the test results were illustrated in **Figure 10**.

A decantation bed thickner was used in compost sorption process was tested at a scale of 2–3 kg/h; collecting operational and design data to build an industrial installation. A technological diagram of the compost washing at three stage process developed unit was made. Activated shale destruction almost observed at third cycled end. Heavy metal concentration change increased from 2nd cycle with performance of 60–70% and also simultaneous dilution of waste mud products by sedimented. it is necessary to optimize the cycling stages on metal circulation without the metal concentration change.

5.1 Sorbent composite char/salt method

These cheap alkali sorbent fines may be so feasible at the side of cost and sorbent production. The high amount toxicity of hazardous waste slurries of cyanide in recovery of Au and hot water streams might be reduced by massive alkali sorbent use [13]. Advanced column washing by char of Turkish lignite and wood char may be feasible. However, the washing with solid expanded clay soaked alkali fine char of Turkish lignites can be utilized [14]. The heavy metal and toxic contaminants of waste waters, nitrates nitrites pesticides and Hg with clay soaked at high elimination rates ranging 52–64%.

The approach of sorption kinetics assumed basically that the process exponentially was developed itself, as seen in **Figure 8** with specific features. The elimination of Pb and Hg in waste waters with clay compost sorbent was a decisive sorbent for the reaction path on the kinetics of washing acidic mine waters. Therefore a static model of washing decantation was developed at 1 mm of coal sand size. Linstead of fluid bed combustion, packed bed column of coarse size composts and

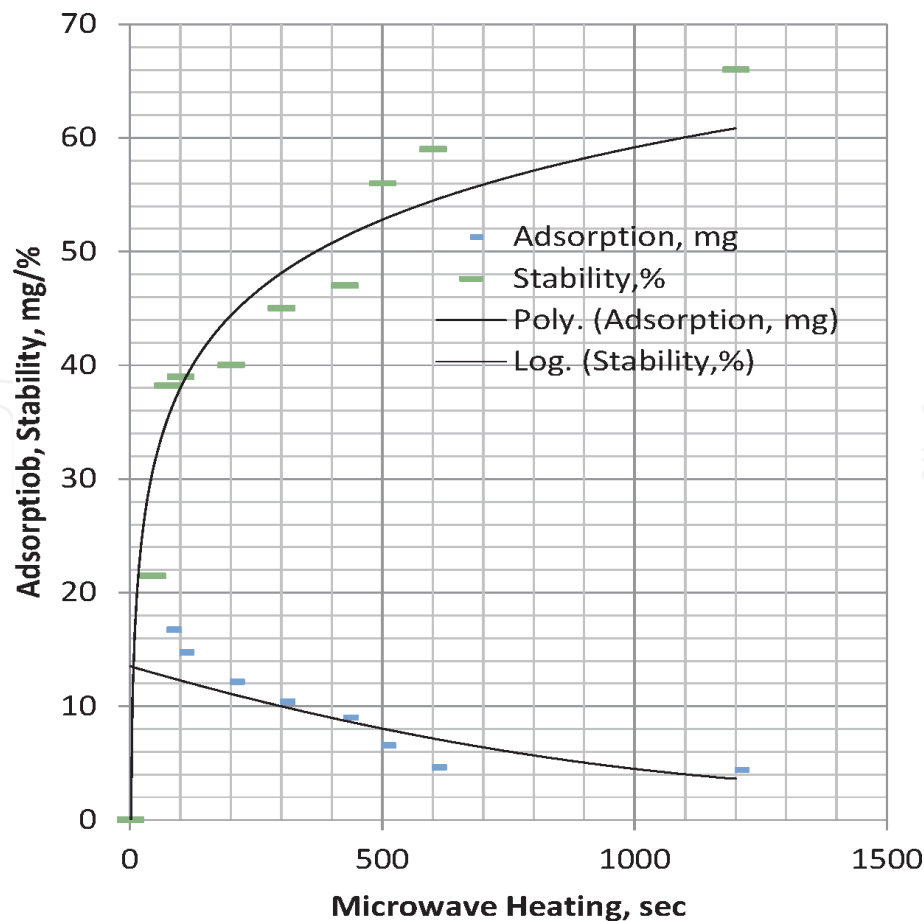


Figure 14.
Thermal stability of raw and activated bentonites with chlorite of char shale.

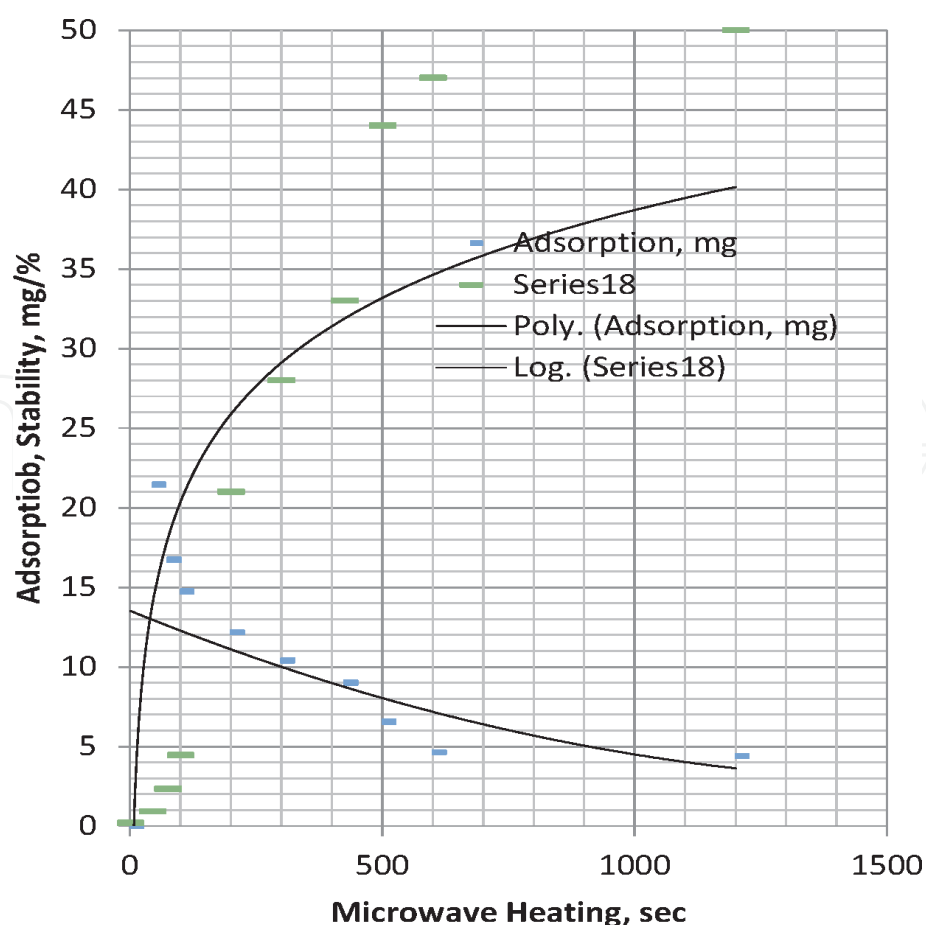


Figure 15.
Thermal sorption quality and activated zeolite with chlorite of char shale.

packages was highly governed by slow washing, sufficiently sorption of toxic sludges.

As seen in **Figure 13**, the activated clay - zeolite examined was more efficient as an absorbent for a conversion of waste waters to friendly waters. It can be a promising waste contaminated waters, municipal wastes because of high activity in the collection and leaching in the toxic solutions in the mine waters and lakes. The sorption rates reached to 74% with Şımak asphaltite shale and zeolite compost.

However, due to the presence of salt in the environment, the bentonite particles which have become dispersed and suspended must coagulate and collapse along with other large nasties, as the surface loads decrease to absolute value and approach zero load point. The high decreases in the separation efficiency in the FeCl₃ medium observed in **Figure 14**.

The activation decreased in ambient pH. So, the most important ions in the bentonites are H⁺ and OH⁻. Therefore, the changes that may occur in pH especially at low pH H⁺ ion adsorbed the bentonite particles to the surface and makes the surface neutral to facilitate coagulation, so the bentonite particles which are to be suspended in the precipitation conditions are also collapsed and the separation efficiency is degraded at low pH. It has been reflected as seen in **Figures 14 and 15**.

The ability of the Na⁺ ion to hydrate and especially the Ca²⁺ cation to take its place easily is an important consideration.

6. Conclusions

The corresponding increase in surface area can improve the removal of impurities in the sample due to the microwave dissolved acid treatment over zeolite/

asphaltite char shale and bentonite applied and by the replacement of the inter-changeable cations by the H⁺ cation. The increase in the surface area of the bentonite type after acid modification heavy metal sorption 54%.

As the acid molarity increased, it was determined that the acid-modified Bentonite (0.84 ppm) and Zeolite (0.69 ppm) samples adsorbed more Pb than the natural form B (0.66 ppm).

Due to the removal of octahedral cations after acid activation, the formation of new acid sites in the clay lamella structure increased the specific surface area and porosity. Therefore, the structure of bentonite showed more Pb and Fe adsorption properties. In this study, the Pb adsorption capacity of bentonite samples prepared with 100 min circulation was found to be the sufficient washing.

Analyzes were performed using approximately 30 mg of sample at a temperature range of 30–1000°C at a heating rate of 10°C/min. The temperature ranges and mass loss values obtained from the TG analysis are given in **Table 6**. The endothermic peaks observed in the DTA curves of the natural Bentonite, char shale and zeolite samples at 105, 299 and 98°C, respectively. There are due to the removal of physically adsorbed water.

The shift of endothermic peak temperatures to lower values with increasing acid concentration was also observed. TGA analysis of natural bentonite, coal char shale and zeolite samples revealed that the total mass losses at 1000°C were 9.19%, 47.75% and 8.15%, respectively.

This high divergence was the endothermic peak at 150°C in DTA. In addition, in the TGA curve, a mass loss of 4.3% at 200–320° C is the endothermic peak at 270°C in DTA. This mass loss is due to the removal of hydrate and sulphate bound to Brønsted acid centers. In addition, mass loss of 4.9% in the range of 390–650°C due to dehydroxylation of the crystal lamella layers is in the form swelling easily on an endothermic peak of 621°C centered on DTA.

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.

In the thre stage microwave activated washing test measurements made with tap water, it was found that 73 mg/l (ppm) in bentonite/asphaltite char shale decreased to 53 mg/l (ppm)/in last column output. Likewise, the washed waste waters obtained after 100 min washing by microwave activaty using sodium salts softened flow with 1 mm sorbent packages showed reductions in Pb, Hg and Fe at 47% performance.

In clean water aliquate had the 24 ppm Pb,5 ppm Hg and 57 Fe values, which Pb reduction rates of sorption at Langmuir model with nitrate washed, was 0,73 ppm/min.l, Hg and total Fe reduction rate has decreased to 0,43 ppm/min.l and 0,23 ppm/min.l, respectively.

	SiO ₂	Al ₂ O ₂	Fe ₂ O ₂	MgO	K ₂ O	CaO	TiO ₂	LOI*
Kaolin (%)	47.85	37.60	0.83	0.17	0.97	0.57	0.74	11.27
Şırnak Asphaltite Char Shale	47.85	37.60	0.83	0.17	0.97	0.57	0.74	11.27
Bentonite	47.85	37.60	0.83	0.17	0.97	0.57	0.74	11.27
Marly Shale	47.85	37.60	0.83	0.17	0.97	0.57	0.74	11.27
Zeolite	47.85	37.60	0.83	0.17	0.97	0.57	0.74	11.27

*LOI: Loss on Ignition at 1000°.

Table 6.
Sorbent Clay Types for waste water treatment.

The swelling index and viscosity studies of compost bentonite and zeolite did not changed in packed columns washing filtered through steel meshed packages during microwave act washing.

The pH increased at washing was efficient in heavy metal sorption, the swelling index decreased, the loss of filtration increased negatively, and viscosity decreased by the addition of sodium.

In the obtained data, it was observed that sorption manner of bentonite has negatively effected by foreign ions in washing water for the activation especially total iron ion.

This result also indicated that the properties of the irrigation and fish farming water to be used during wet soil amendment of of agricultural organic soil and lake muds with wet bentonites, on waste water treatment units which friendly mud should be controlled, otherwise the contamination after discharge would be harm human health, toxicology of animal and fish feed.

Abbreviations

Greek symbols

a	affinity parameter of the Langmuir isotherm (L mg^{-1})
b	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, $0 < r < R_p$ (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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References

- [1] Nalbantcilar, MT, Pinarkara, SY, 2016, Public health risk assessment of groundwater contamination in Batman, Turkey, *Water Health*. 2016 Aug;**14**(4): 650-61. doi: 10.2166/wh.2016.290.
- [2] Çelik, R., 2015, Temporal changes in the groundwater level in the Upper Tigris Basin, Turkey, determined by a GIS technique, *Journal of African Earth Sciences*, Volume 107, July 2015, Pages 134–143
- [3] Disli, E., 2017, Hydrochemical characteristics of surface and groundwater and suitability for drinking and agricultural use in the Upper Tigris River Basin, Diyarbakir—Batman, Turkey, Springer, 2017, *Environmental Earth Sciences* **76**(14), DOI: 10.1007/s12665-017-6820-5
- [4] S. Ahamed, A. Hussam, A.K.M. Munir, 2009, Groundwater Arsenic Removal Technologies Based on Sorbents: Field Applications and Sustainability, *Handbook of Water Purity and Quality*, Academic Press, Amsterdam (2009) 379–417
- [5] J.S. Ahn, C.M. Chon, H.S. Moon, K. W. Kim, 2003, Arsenic removal using steel manufacturing by-products as permeable reactive materials in mine tailing containment systems, *Water Research*, **37** (2003), pp. 2478–2488
- [6] J.P. Allen, I.G. Torres, 1991, Physical separation techniques for contaminated sediment, N.N. Li (Ed.), *Recent Developments in Separation Science*, CRC Press, West Palm Beach, FL (1991)
- [7] S.J. Allen, L.J. Whitten, M. Murray, O. Duggan, 1997, The adsorption of pollutants by peat, lignite and activated chars, *Journal of Chemical Technology & Biotechnology*, **68** (1997), pp. 442–452
- [8] E. Álvarez-Ayuso, H.W. Nugteren, 2005, Purification of chromium(VI) finishing wastewaters using calcined and uncalcined Mg-Al-CO₃-hydrotalcite, *Water Research*, **39** (2005), pp. 2535–25
- [9] R.A.I. Abou-Shanab, J.S. Angle, R.L. Chaney, 2006, Bacterial inoculants affecting nickel uptake by *Alyssum murale* from low, moderate and high Ni soils, *Soil Biology and Biochemistry*, **38** (2006), pp. 2882–2889
- [10] R.A. Abramovitch, B.Z. Huang, M. Davis, L. Peters, 2003, In situ remediation of soils contaminated with toxic metal ions using microwave energy, *Chemosphere*, **53** (2003), pp. 1077–1085
- [11] J. Acharya, J.N. Sahu, C.R. Mohanty, B.C. Meikap, 2009, Removal of lead(II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation, *Chemical Engineering Journal*, **149** (2009), pp. 249–262
- [12] J. Acharya, J.N. Sahu, B.K. Sahoo, C.R. Mohanty, B.C. Meikap, 2009, Removal of chromium(VI) from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride, *Chemical Engineering Journal*, **150** (2009), pp. 25–39
- [13] Novak, I., Cícel, B. 1978. Dissolution of smectites in hydrochloric acid; II, Dissolution rate as a function of crystallochemical composition. *Clays and Clay Minerals*, **26**, 341–344.
- [14] Önal, M., Sarıkaya, Y., Alemdaroglu, T., Bozdoğan, I. 2002. The effect of acid activation on some physicochemical properties of a bentonite. *Turkish Journal of Chemistry*, **26**, 409–416
- [15] Srasra, E., Bergaya, F., van Damme, H., Arguib, N.K. 1989. Surface properties of an activated bentonite. Decolorization of rape-seed oil. *Applied Clay Science*, **4**, 411–421.

- [16] Srivastava, R.V. 2003. Controlling of SO₂ Emissions, A Review of Technologies, Nova Science Publishers, Inc., New York, 1 pp.
- [17] Venaruzzo, J.L., Volzone C., Rueda M.L., Ortiga J. 2002. Modified bentonitic clay minerals as adsorbents of CO, CO₂ and SO₂ gases. *Microporous and Mesoporous Materials*, **56**, 73–80.
- [18] Alemdaroglu, T., Akkus, G., Önal, M., Sarikaya, Y. (2003). Investigation of the Surface Acidity of a Bentonite Modified by Acid Activation and Thermal Treatment. *Turkish Journal of Chemistry*, **27**, 675–681.
- [19] Benesi, H.A. (1956). Acidity of Catalyst Surfaces I. Acid Strength from Colors of Adsorbed Indicators. *The Journal of Physical Chemistry*, **78**, 5490–5494.
- [20] Benesi, H.A. (1957). Acidity of Catalyst Surfaces II. Amine Titration Using Hammett Indicators. *The Journal of Physical Chemistry*, **61**, 970–973.
- [21] Caglar, B., Afsin, B., Tabak, A. (2007). Benzamide Species Retained by DMSO Composites at a Kaolinite Surface. *J. Therm. Anal. Cal.*, **87**, 429–432.
- [22] Caglar, B., Afsin, B., Tabak, A., and Eren, E. (2009). Characterization of Cation Exchanged Bentonites by XRPD, ATR, DTA/TG and BET measurement Investigation of. *Chemical Engineering Journal*, **149**, 242–248.
- [23] Chitnis, S.R., Sharma, M.M. (1997). Industrial Applications of Acid-Treated Clays as Catalyst. *Reactive and Functional Polymers*, **32**, 93–115.
- [24] Christidis, G.E., Scott, P.W., Dunham, A.C. (1997). Acid Activation and Bleaching Capacity of Bentonites from the Islands of Milos and Chios, Aegean, Greece, *Appl. Clay Sci.*, **12**, 329–347.
- [25] Flessner, U., Jones, D.J., Roziere, J., Zajac, J., Storaro, L., Lenarda, M., Pavan, M., Lopez, A.J., Castellon, E.R., Trombetta, M., Busca, G. (2001). A Study of the Surface Acidity of Acid-Treated Montmorillonite Clay Catalyst. *J. Mol. Catal. A: Chemical*, **168**, 247–256.
- [26] Heyding, R.D., Ironside, R., Norris, A.R., ve Prysiazniuk, R.Y. (1960). Acid Activation of Montmorillonite. *Can. J. Chem.*, **38**, 1003–1016.
- [27] Hutson, N.D., Hoekstra, M.J., Yang, R.T. (1999). Control of Microporosity of Al₂O₃-Pillared Clays: Effect of pH, Calcination Temperature and Clay Cation Exchange Capacity. *Micropor. Mesopor. Mater.*, **28**, 447–459.
- [28] Volzone, C., Ortiga, J. 2009. Adsorption of gaseous SO₂ and structural changes of montmorillonite. *Applied Clay Science*, **44**, 251–254
- [29] Noyan H, Önal M, Sarikaya Y. The Effect of Sulphuric Acid Activation on the Crystallinity, Surface Area, Porosity, Surface Acidity, and Bleaching Power of a Bentonite. *Food Chemistry*. 2007;**105**: 156-163
- [30] Önal M, Sarikaya Y, Alemdaroğlu T, Bozdoğan İ. The Effect of Acid Activation on Some Physicochemical Properties of a Bentonite. *Turkish Journal of Chemistry*. 2002;**26**:409-416
- [31] Reedy, C.R., Nagendrappa, G., Prakash, B.S.J. (2007). Surface Acidity Study of Mn⁺-Montmorillonite Clay Catalysts by FT-IR Spectroscopy:
- [32] Rodriguez MAV, Barrios MS, Gonzalez JDL, Munoz MAB. Acid Activation of a Ferrous Saponite (Griffithite): Physico-Chemical Characterization and Surface Area of the Products Obtained. *Clays and Clay Minerals*. 1994;**42**:724-730