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Removal of metals and metalloids from acidic mining lake (AML) using olive oil solid waste (OSW)

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Abstract

The acidic mining lakes have low pH values and high metal and metalloid concentrations. In this study, the ability of low-cost olive oil solid waste (OSW) to remove Al, As, Cd, Fe, B and Ti ions from aqueous solutions in short term has been evaluated. Adsorption capacities (mg g⁻¹) of OSW (1:5–1:10 w/v) were 764.06–411.75 for Al, 0.26 for As, 0.07–0.14 for Cd, 2181.5–2406.5 for Fe, 23.70–82.50 for B and 0.12–0.0.34 for Ti. OSW addition increased acidic mine water (AMW) pH from 2.41 to 3.2 with 1:5 and from 2.41 to 2.7 to 1:10 mixing ratio, respectively, after 10 min. The best gradual decrease has been observed with different ratio of OSW applications on B and Ti concentrations. OSW adsorbs 32.41% and 62.68% of B at the ratio of 1:5 and 1:10 and 55.29% and 83.04% of Ti at the ratio of 1:5 and 1:10 (OSW:AMW) mixtures, respectively. The results show that OSW has great potential for metal removal from acidic mine water.

Keywords Adsorption · Olive oil solid waste · Heavy metal/metalloid · Acidic mine lake

Introduction

It is known that oxidation of sulfur bearing minerals is responsible for the formation of low pH waters. This event is typically observed in mining activities, which results in the formation of acid mine drainage (AMD) from underground galleries to surface waters or in the creation of acidic mining lakes (AML) within the surface depressions of abandoned open-pit mines. AMLs are commonly observed in the open-pit coal mining sites in Central Europe and Northern America where lignite reserves are found close to ground surface. Hundreds of such AMLs are found in the Lusatia region of Germany (Friese et al. 1998; Yucel et al. 2014; Wisotzky and Obermann 2001; Karakas et al. 2003; Yucel and Baba 2013), and numerous researches have been conducted on their formations and characteristics (Blodau 2006; Evangelou 1998).

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AMLs have low pH values and high metal and metalloid concentrations (Gunduz et al. 2007; Yucel et al. 2016). It has been previously reported that pH values ranged from 2 to 4 and electrical conductivity values reach up to 5000 μS⁻¹ cm (Yucel et al. 2014; Blodau 2006; Evangelou 1998). These low pH values cause elevated concentrations of metals/ metalloids and toxic elements such as Cr, Al, Cd, Mn, As, Zn and Ni. Drainage water from AMLs can destruct downstream aquatic life. Besides degraded water quality, acidic mining lakes are also responsible for landslides by dissolving carbonate minerals in soil (Geller et al. 1998; Schultze and Geller 1996). There are number of AMLs in the Can Coal District in Canakkale, Turkey (Fig. 1). The area is rich in lignite, which is currently being utilized in a 2×160 MW capacity thermal power plant and in domestic heating of the surrounding residential areas. There are also numerous small-scale private companies that extract coal from a number of sites in the region. When the depression cones of these open pits are filled with surface and subsurface drainage, numerous AMLs with variable sizes are formed (Baba et al. 2009; Yucel et al. 2014). pH of these lakes are generally lower than 4 and accumulate metals such as Al, Fe, Mn. The limnological and hydrogeochemical characteristics of AML (Gunduz and Baba 2008; Gunduz et al. 2007; Yucel and Baba 2013; Yucel et al. 2014) were studied in detail. Yucel and Baba (2016) reported that if sulfur content of a









Fig. 1 Acidic mine lake in Biga Peninsula

rock > 0.3%, it oxidizes rapidly and may produce AMD. The paste pH of the mine wastes was between 2.3 and 3.8, which were similar to pH value of AML water in the region.

Acidic mine lakes have brown reddish color caused by dissolution of iron hydroxides. If such lakes are not rehabilitated, they lead to contamination of surface and groundwater resources (Gunduz and Baba 2008). Reclamations of such lakes with current treatment technologies are expensive; therefore, there is an urge to find out other materials. Many technologies, including reverse osmosis and ion-exchange resin, have been used to remove heavy metals and harmful metalloids from aqueous solution. The most commonly used technology for active treatment is chemical neutralization. Liming is a common and effective treatment practice to neutralize acidity and precipitate heavy metals. However, this method of treatment becomes expensive due to the extensive period during which treatment is required (MEND 1994). The adsorbents can be mineral, organic, zeolites, industrial and agricultural by-products and wastes (Kurniawan et al. 2006). The lists of some materials that can be used as lowcost absorbents for metal and metalloid removal from aqueous solutions are summarized in Table 1.

Treatment of AMD by passive methods is grouped in four categories: anoxic limestone drain, neutralization, biosorption, bioreactors and wetland treatment. There are some criteria to select the best biosorption materials such as the treatment of AMD should not create environmental problems, materials used for AMD treatment should be renewable, materials should be readily available and material should be economic (Bechard 1993). Several ways to accumulate and bind pollutants by organic materials have been reported by Veglio and Beolchini (1997).

Turkey is an important olive producer and production of olive for oil extraction in 2015 was 1.3×10^6 tons in Turkey (TUİK 2015). Approximately 75% of trees were grown for olive oil production and 25% for table olive production

in Turkey (TUIK 2015). About 26% of Turkey's total olive production is produced from Marmara region (study area). Olive oil solid waste (OSW) is a by-product which can also cause storage problems. Little amounts of OSW are used as organic fertilizer (İlay et al. 2013), fodder, and additive in animal food. OSW can also be used as a low-cost adsorbent.

The use of agricultural and organic by-products in bioremediation of heavy metals is known as biosorption (Gupta et al. 1998, 2012a; Gupta and Saleh 2013). Biosorption of metals and metalloids by agricultural and industrial wastes is used in water treatment. Red mud (Nadaroglu et al. 2010) is largely produced from the alumina industry. De-oiled soya was used as an adsorbent for removal of toxic dyes from wastewater (Mittal et al. 2009, 2010). Hasan et al. (2000) reported that rubber-wood ash was good adsorbent for the Ni(II) cation from dilute solution. The maximum adsorption for nickel was 0.492 mmol g⁻¹ at pH 5 and 30 °C. Balarak et al. (2015) used canola residues to remove methylene blue from aqueous solution, and the maximum dye removal was obtained to be 97.5%. Photocatalytic treatment can be used to reduce water pollution caused by dyes (Saravanan et al. 2013a, b). The photocatalytic activity of ZnO modified with CdO successfully degraded methylene blue under visible light (Saravanan et al. 2011, 2015). Martínez et al. (2006) used by-product of wine production for sorption of lead and cadmium from aqueous solutions. They reported that, at pH 5.5, maximum sorption capacities of grape stalk was 0.241 and 0.248 mmol g⁻¹ for Pb(II) and Cd(II), respectively. HCl or EDTA solutions were successful to desorb lead from the grape stalks.

Amin et al. (2006) used rice husk to desorb arsenic from aqueous solution. Six grams of rice husk was mixed with $100 \mu g L^{-1}$ As containing solution at a pH range of 6.5–6.0. About 71–96% desorption was observed with KOH-treated rice husk. Besides modified cellulose materials, walnut hull was also good absorbent (Wang et al. 2009) for chromium





Table 1 Metal/metalloids adsorption capacities for some low-cost adsorbents

Material	Metal/metalloid	Adsorption capacities (mg g ⁻¹)	References		
Fly ash	В	20.9	Oztürk and Kavak (2005)		
Montmorillonite	Cu(II)	3.0	Abollino et al. (2003)		
Cocoa shells	Pb(II)	6.2	Meunier et al. (2003)		
Cork wastes	Pb(II)	13.46	López-mesas et al. (2011)		
Organophilic bentonite	Cd(II)	2.8	Andini et al. (2006)		
Hazelnut shell	Ni(II)	10.1	Demirbas et al. (2002)		
Tobacco dust	Zn(II)	25.1	Qi and Aldrich (2008)		
Peanut hulls	Cu(II)	65.6	Periasamy and Namasivayam (1996)		
Orange peel (citrus reticulate)	Ni(II)	80.0	Ajmal et al. (2000)		
Grape stalk waste	Ni(II)	10.6	Villaescusa et al. (2004)		
	Cu(II)	10.1			
	Cd(II)	0.24 *	Martinez et al. (2006)		
Coffee beans	Cd(II)	0.058*	Kaikake et al. (2007)		
Grape stalk	Cu(II)	42.92	Escudero et al. (2008)		
	Ni(II)	38.31			
Apple residues	Cd(II)	0.158	Lee et al. (1998)		
Tobacco (dust cultural waste)	Pb(II)	39.6	Qi and Aldrich (2008)		
Sugar beet pulp	Pb(II)	73.8	Reddad et al. (2003)		
Olive pomace	Cd(II)	0.030	Martín-Lara et al. (2008)		
Tree bark	Cu(II)	21.6	Gaballah and Kilbertus (1998)		
Banana peel	Cu(II)	0.075	Kurniawan et al. (2006)		
Olive cake	Cd(II)	65.35	Al-Anber and Matouq (2008)		
Tea factory waste	Cr(VI)	54.65	Malkoc and Nuhoglu (2007)		
Grape bagasse	Cd(II)	0.479	Farinella et al. (2007)		
Palm tree leaves	Zn(II)	14.7	Abu Al-Rub (2006)		
Rubber-wood		0.492*	Hasan et al. (2000)		
Cotton cellulose	B(III)	11.3	Liu et al. (2007)		
Apple residue	Cu(II)	0.170	Lee et al. (1998)		
Rice bran	Zn(II)	14.17	Wang et al. 2006		
Brewery waste	Pb(II)	33.1-1656	Can and Jianlong (2008)		
•	Ag(I)	17.3-864	5 . ,		
Carrot residue	Cu(II)	0.515	Nasernejad et al. (2005)		
Crab shell	Cu(II)	243.9	Vijayaraghavan et al. (2006)		
	Co(II)	322.6			
Maize cob and husk	Zn(II)	495.9	Iqwe et al. (2005)		
	Pb(II)	456.7	• , ,		
	Cd(II)	493.7			
Olive pomace	Cu(II)	0.180*	Martín-Lara et al. (2008)		
Active carbon from oat hulls	As	1.57-3.09	Chuang et al. (2005)		
Olive solid waste (OSW)	Al(III)	764.05–411.75	This study		
	As	0.26	•		
	Cd(II)	0.079-0.142			
	Fe	2181.5-3406.5			
	В	23.70–82.50			
	Ti	0.128-0.348			

 $[*]mmol \; g^{-1}$



(VI). Optimum pH for removal was 1.0, while chromium (VI) removal was 97.3% (Wang et al. 2009). The removal increased with adsorbent concentration and the decrease in adsorbate concentration. Gharaibeh et al. (1998) reported that olive oil by-products were efficient for zinc and lead removal from aqueous solutions. Removal of heavy metals and metalloids from contaminated water is very important for environmental health (Weng and Huang 2004). Conventional technologies for the removal of heavy metal such as chemical precipitation, membrane separation, reverse osmosis, adsorption and emulsion per traction technology (Zhou et al. 1993; Naiya et al. 2009; Ali 2010, 2012; Ali et al. 2012; Gupta et al. 2011, 2012b, 2013). Saravanan et al. (2016) suggested that PANI/ZnO nanocomposite can be used for environmental remediation. Many methods have been studied to develop much more cheaper and effective technique for removal of metals and metalloids from wastewater and adsorption was the most effective method for removal of heavy metal if combined with appropriate regeneration steps (Naiya et al. 2009; Khan et al. 2011; Ali et al. 2016, 2017).

The aim of this study is to investigate the possible use of olive oil solid waste (OSW) as a low-cost and reachable adsorbent for the removal of toxic metals and metalloids from acidic mine lakes which can be seen in different part of world such as Biga Peninsula.

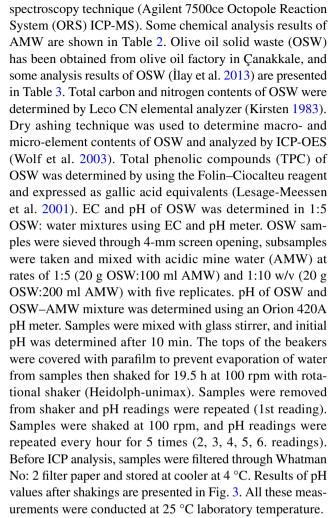
Materials and methods

Study area

The Çan Coal District is located in Biga Peninsula in North Western Turkey. It is located about 100 km away from Çanakkale. The Çan Coal District has been in operation since 1980s, and lignites are being extracted in the region. Acidic lakes can be seen around this region where agriculture especially olive and olive oil productions are an important part of economy. As a result, high amount of olive oil waste are generated that can cause storage problems. Paleozoic-aged metamorphic rocks are the basement of the study area. Volcanic rocks are altered and fractured due to the effects of active faults in the region (Fig. 2). Many industrial metals and some precious metals have been detected in the altered volcanic rocks (Baba and Gunduz 2010; Baba et al. 2009).

Methods

100 mL sample was taken from AML water for heavy metals and metalloids analysis. AML samples were filtered through 0.45- μ m filter paper and stored in refrigerator at 4 °C. 0.5 N HNO₃ was added to samples to reduce sample pH below 2 and analyzed by inductively coupled plasma-mass



Surface area measurements were performed on Quantachrome Quadrasorb SI surface area analyzer. The samples were out-gassed for 3 h under nitrogen prior to adsorption measurement. The specific surface area of OSW was determined by applying the BET method. OSW was ground with grinder, and sieved to 0.5 mm particle size and sample weight was 0.34 g.

Heavy metals and metalloid absorptions of OSW at 1:5 and 1:10 AMW have been calculated according to Eq. (1)

$$q = \left[\left(C_i - C_f \right) * V \right] / W \tag{1}$$

where q = (amount of adsorbate, adsorbed in mg)/(amount of adsorbent used for adsorption in g). C_i is the initial concentration of heavy metals and metalloid (mg L⁻¹); C_f is final heavy metals and metalloid concentrations of solution (mg L⁻¹); V is final total volume in the reactor (L); W is the amount of OSW used for biosorption test (g) (*density of OSW was 0.8 g cm^{-3}).

SPSS 17 package program has been used for statistical analysis. Differences among treatments were determined by ANOVA; comparisons were made by Post Hoc Test.





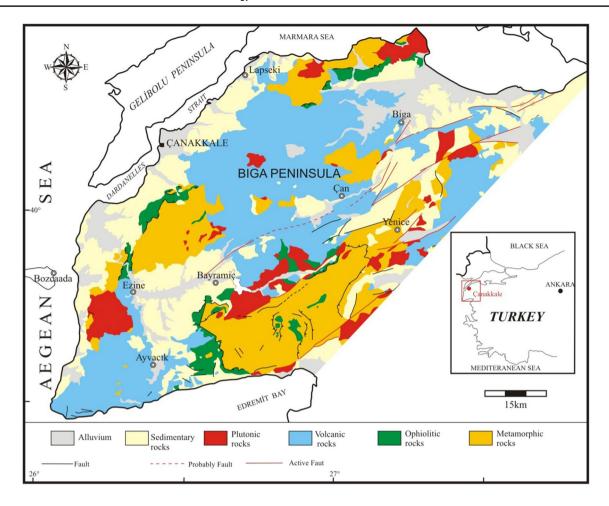


Fig. 2 Geological map of Biga Peninsula (Baba and Gunduz 2010, modified from General Directorate of Mineral Research, Exploration 2002)

Results and discussion

OSW has low pH (5.7), high Fe (1243.91 mg kg⁻¹) content and surface area of OSW was 0.545 m² g⁻¹ (Table 3). Descriptive statistical results are presented in Tables 4 and 5. The results of heavy metals and metalloids concentrations after treatment of AMW are presented in Figs. 4, 5 and 6. AMLs have low pH values and high metal and metalloid concentrations (Gunduz et al. 2007; Yucel et al. 2016).

Addition of OSW to AMW increased pH from 2.41 to 3.2 with 1:5 and from 2.41 to 2.7 with 1:10 mixing ratio, respectively, after 10 min (Fig. 3). The increase in pH can be caused by either adsorption of acidic metals by OSW or release of basic elements from OSW. OSW applications reduced Al, As, Cd, Fe, B and Ti concentrations in AMW which resulted with the increase in mixture pH. Increasing pH in AMW:OSW mixtures reduced most of the metals and metalloid concentrations except As. Al and Fe concentration reduced with 1:5 OSW which had higher solution pH. B, Ti and Cd concentrations reduced in AMW:OSW mixtures compared to AMW alone (pH:2.41, Fig. 3).

Heavy metals and metalloid adsorption capacities of OSW are presented in Table 6. Except Al, all cations were effectively adsorbed by 1:10 (OSW:AMW) mixture. Al concentration of AMW reduced from 273 to 150.75 mg L⁻¹ when it was mixed with 1:5 (OSW:AMW) mixture (Fig. 4a). OSW: AMW (1:5) treatment reduced Al concentration of AMW about 45%, while 1:10 (OSW:AMW) treatment reduced 13% (Fig. 4a).

On the other hand, 1:5 (OSW:AMW) mixture had no significant effect on As reduction from AMW (Table 4 and Fig. 4b). 1:10 (OSW:AMW) mixture application reduced As concentration of AMW about 22% compared to initial value (p < 0.05).

OSW application dramatically reduced Fe concentrations of AMW (Fig. 5a). Average initial Fe concentration was 411 mg L⁻¹, and it reduced to 61.95 mg L⁻¹ with OSW addition (1:5). OSW treatments reduced Fe concentrations 84.92% and 73.67% with 1:5 and 1:10 (OSW:AMW) mixtures, respectively (Fig. 5a). Iron content of OSW was originally higher than those of AMW (Tables 2 and 3). When AMW amount increased from 1:5 to 1:10 (OSW:AMW)



Table 2 Chemical properties of AMW

Properties	Value		
pH	2.41		
Li*	0.599		
В	11.7		
Na	210		
Mg	160		
Al	273		
K	1100		
Ca	65.5		
Cr	0.0167		
Mn	57.7		
Fe	409		
Co	2.37		
Ni	1.12		
Cu	0.144		
Zn	10.6		
Ga	0.019		
As	0.103		
Sr	2.55		
Cd	0.0329		
Ba	0.102		
Ti	0.0373		
Pb	0.0134		

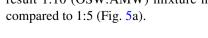
*Concentrations of all metal and metalloids are given in $mg L^{-1} unit$

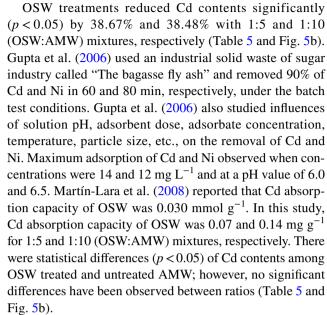
Table 3 Chemical properties of the OSW (İlay et al. 2013)

Parameters	Value
pH	5.7 ± 0.04
EC (μ S cm ⁻¹)	822 ± 2
N (%)	1.12 ± 0.06
P (%)	0.04 ± 0.00
K (%)	0.57 ± 0.00
Ca (%)	0.5 ± 0.02
Mg (%)	0.06 ± 0.00
$B (mg kg^{-1})$	16.9 ± 0.55
Fe (mg kg^{-1})	1243.91 ± 75.61
$Mn (mg kg^{-1})$	32.75 ± 1.99
$Zn (mg kg^{-1})$	17.34 ± 3.15
C (%)	49.1 ± 0.75
TPC ($mg kg^{-1}$)	1.20 ± 0.01
C/N	43.8 ± 1.86
BET surface area (m ² g ⁻¹)	0.545

TPC total phenolic compounds

mixture, soluble Fe of OSW released into the water. As a result 1:10 (OSW:AMW) mixture has higher Fe content





Agricultural by-products bind heavy metals by adsorption, chelation and ion exchange (Gardea-Torresdey et al. 1996; Sun and Shi, 1998). Igwe et al. (2005), investigated that the adsorption of Pb²⁺, Cd²⁺ and Zn²⁺ ions from solutions by unmodified and modified maize cob and husk. Maximum adsorption occurred at 495.9, 456.7 and 493.7 mg g⁻¹ for Zn²⁺, Pb²⁺ and Cd²⁺ ion, respectively, without modification.

B and Ti concentrations were lower in 1:10 (OSW:AMW) mixture than those in 1:5 ratio (Fig. 6a, b). Liu et al. (2007) reported that with higher pH, there was lower removal of boron by cotton cellulose. Therefore, increasing AMW resulted in lower solution pH and lower B and Ti removal. Instead of increasing sorbent amount, perhaps solution pH can be increased to enhance removal capacity of OSW.

The best gradual decrease has been observed with different ratio of OSW applications on B and Ti concentrations (Fig. 6b). OSW adsorbs 32.41% and 62.68% of B at the ratio of 1:5 and 1:10, respectively. OSW adsorbs 55.29% and 83.04% of Ti at the ratio of 1:5 and 1:10 (OSW:AMW) mixtures, respectively (Fig. 6b).

Several organic materials used to treat AMW according to local availability such as composts produced from cow manure, sawdust, straw (Vile and Wieder 1993). They reported that AMW quality in compost wetlands is improved by filtration of colloidal materials and adsorption of metals by the organic matrix. In general, biologically mediated Fe(II) reduction occurred and caused alkalinity (Vile and Wieder 1993).

Agricultural waste and other agricultural by-products have been used to remove heavy metals from aqueous medium (Kelly-Vargas et al. 2012; Hegazi 2013; Kadirvelu et al. 2001; Hamza et al. 2013). Carrot residues were





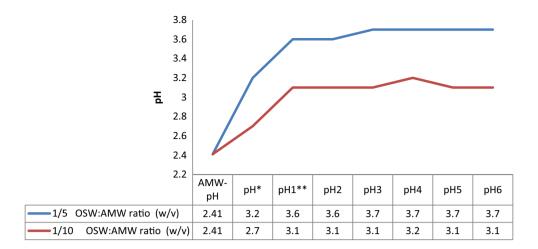


Fig. 3 Changes of pH as a function of time during the experiments (OSW:AMW mixture of 1 g/5 ml and 1 g/10 ml) with starting pH of 2.41. *10 min. after mixing, **19.5 h after mixing of OSW and

AMW, interval among other pH readings were 1 h (last pH reading (pH6) was done 24.5 h after first reading)

Table 4 Descriptive statistics of metal/metalloids concentrations (mg L⁻¹) in AMW:OSW mixtures

Metals and metalloids	Applications	N	Mean	Std. error	Minimum	Maximum	Significant
Al	AMW	4	272.950	0.484	271	274	p < 0.05
	AMW:OSW (1:5)	4	150.750	21.800	112	210	
	AMW:OSW (1:10)	5	236.400	3.326	229	248	
As	AMW	4	0.103	0.001	0.100	0.100	p < 0.05
	AMW:OSW (1:5)	4	0.104	0.006	0.090	0.110	
	AMW:OSW (1:10)	5	0.080	0.006	0.060	0.090	
Fe	AMW	4	411.000	1.225	408.000	414.000	p < 0.05
	AMW:OSW (1:5)	4	61.950	6.989	50.900	80.200	
	AMW:OSW (1:10)	5	108.200	2.709	102.000	115.000	
Cd	AMW	4	0.033	0.000	0.030	0.030	p < 0.05
	AMW:OSW (1:5)	4	0.020	0.003	0.020	0.030	
	AMW:OSW (1:10)	5	0.020	0.001	0.020	0.020	
В	AMW	4	11.700	0.108	11.400	11.900	p < 0.05
	AMW:OSW (1:5)	4	7.908	0.646	6.660	9.640	
	AMW:OSW (1:10)	5	4.366	0.049	4.200	4.490	
Ti	AMW	4	0.037	0.001	0.040	0.040	p < 0.05
	AMW:OSW (1:5)	4	0.017	0.002	0.010	0.020	
	AMW:OSW (1:10)	5	0.006	0.000	0.010	0.010	

used as a biosorbent for heavy metal removal. Carboxylic and phenolic functional groups were responsible for the cation exchange capacity of carrot residue (Nasernejad et al. 2005). Pagnanelli et al. (2003) used olive solid waste biosorption of Cu, Pb and Cd. They concluded that carboxylic and phenolic groups were responsible for metal removal by a surface complexation mechanism. Therefore, OSW can be a promising, economic and easily available waste to clean AMW from metals and metalloids.

Conclusion

AMW-containing metals and metalloids have been sampled from Biga Peninsula, Çanakkale. Such water poses risk to the environment since they contain elevated concentrations of metals and metalloids. Evaluation of OSW for the metal and metalloid removal from AMW was studied. The results showed that it is possible for reclamation of AMW using olive solid waste. Results indicated that



Table 5 Statistical data of multiple comparisons between groups

Heavy metals and metalloids	(I) 1 (AMW) 2 (1:5) 3 (1:10)	(J) 1 (AMW) 2 (1:5) 3 (1:10)	Mean difference (I–J)	Std. error	Sig.
Al	1.00	2.00	122.20000*	17.214	0.000
		3.00	36.550	16.331	0.147
	2.00	1.00	-122.20000*	17.214	0.000
		3.00	-85.65000*	16.331	0.001
	3.00	1.00	-36.550	16.331	0.147
		2.00	85.65000*	16.331	0.001
As	1.00	2.00	-0.001	0.008	1.000
		3.00	0.02322*	0.007	0.028
	2.00	1.00	0.001	0.008	1.000
		3.00	0.02416*	0.007	0.023
	3.00	1.00	-0.02322*	0.007	0.028
		2.00	02416*	0.007	0.023
Fe	1.00	2.00	349.05000*	6.128	0.000
		3.00	302.80000*	5.813	0.000
	2.00	1.00	-349.05000*	6.128	0.000
		3.00	-46.25000*	5.813	0.000
	3.00	1.00	-302.80000*	5.813	0.000
		2.00	46.25000*	5.813	0.000
Cd	1.00	2.00	0.01267*	0.003	0.002
		3.00	0.01261*	0.002	0.00
	2.00	1.00	-0.01267*	0.003	0.002
		3.00	0.000	0.002	1.000
	3.00	1.00	-0.01261*	0.002	0.00
		2.00	0.000	0.002	1.000
В	1.00	2.00	3.79250*	0.509	0.000
		3.00	7.33400*	0.483	0.000
	2.00	1.00	-3.79250*	0.509	0.000
		3.00	3.54150*	0.483	0.000
	3.00	1.00	-7.33400*	0.483	0.000
		2.00	-3.54150*	0.483	0.000
Ti	1.00	2.00	0.02033*	0.002	0.000
		3.00	0.03067*	0.002	0.000
	2.00	1.00	-0.02033*	0.002	0.000
		3.00	0.01035*	0.002	0.001
	3.00	1.00	-0.03067*	0.002	0.000
		2.00	-0.01035*	0.002	0.001

^{*}The mean difference is significant at the 0.05 level

mixing OSW with AMW at different rates reduced Al, As, Cd, Fe, Ti and B concentrations of water. Results suggested that OSW can remove maximum of 764 mg g⁻¹ of Al, 0.14 mg g⁻¹ Cd, 3406.5 mg g⁻¹ Fe, 82.5 mg g⁻¹ B and 0.35 mg g⁻¹ Ti from AMW. OSW removed Fe more efficiently than other cations with a removal percentage

approximately equal to 85%. Using raw OSW is an alternative method to remove metals and metalloids from AMW. OSW is easily reachable and inexpensive waste material in the Region. Therefore, it can be used easily and quickly in need.



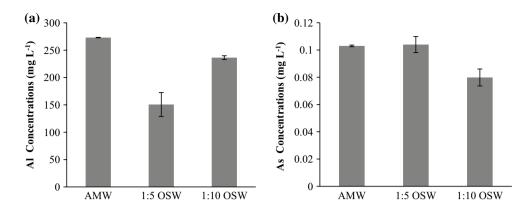


Fig. 4 a, b Al and As concentrations of AMW after OSW treatment

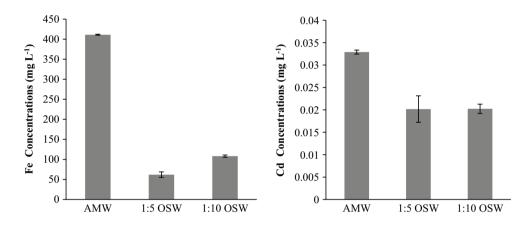


Fig. 5 a, b Fe and Cd concentrations of AMW before and after OSW treatment

Fig. 6 a, **b** B and Ti concentrations of AMW after OSW treatment

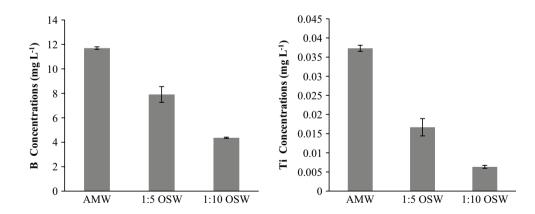


Table 6 Heavy metals and metalloids adsorption capacities (mg g^{-1}) of OSW

OSW:AMW ratio (w/v)	Al	As	Cd	Fe	В	Ti
1:5	764.06	_	0.079	2181.56	23.703	0.128
1:10	411.75	0.260	0.142	3406.5	82.507	0.348



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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Abollino O, Aceto M, Malandrino M et al (2003) Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. Water Res 37:1619–1627. https://doi.org/10.1016/s0043-1354(02)00524-9
- Abu Al-Rub FA (2006) Biosorption of zinc on palm tree leaves: equilibrium, kinetics, and thermodynamics studies. Sep Sci Technol 41:3499–3515. https://doi.org/10.1080/01496390600915015
- Ajmal M, Rao R, Ahmad R, Ahmad J (2000) Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. J Hazard Mater B79:117–131. https://doi.org/10.1016/S0304-3894(00)00234-X
- Al-Anber ZA, Matouq MAD (2008) Batch adsorption of cadmium ions from aqueous solution by means of olive cake. J Hazard Mater 151:194–201. https://doi.org/10.1016/j.jhazmat.2007.05.069
- Ali I (2010) The quest for active carbon adsorbent substitutes, inexpensive adsorbents for toxic metal ions removal from wastewater. Sep Purif Rev 39:95–171. https://doi.org/10.1080/15422 119.2010.527802
- Ali I (2012) New generation adsorbents for water treatment. Chem Rev 112(10):5073–5091. https://doi.org/10.1021/cr300133d
- Ali I, Asim M, Khan TA (2012) Low cost adsorbents for the removal of organic pollutants from wastewater. J Environ Manag 113:170– 183. https://doi.org/10.1016/j.jenvman.2012.08.028
- Ali I, Alothman ZA, Alwarthan A (2016) Synthesis of composite iron nano adsorbent and removal of ibuprofen drug residue from water. J Mol Liq 219:858–864. https://doi.org/10.1016/j.molli q.2016.04.031
- Ali I, Alothman ZA, Alwarthan A (2017) Uptake of propranolol on ionic liquid iron nanocomposite adsorbent: kinetic, thermodynamics and mechanism of adsorption. J Mol Liq 236:205–213. https://doi.org/10.1016/j.molliq.2017.04.028
- Amin N, Kaneco S, Kitagawa T, Begum A, Katsumata H, Suzuki T, Ohta K (2006) Removal of arsenic in aqueous solutions by adsorption onto waste rice husk. Ind Eng Chem Res 45:8105–8110. https://doi.org/10.1021/ie060344j
- Andini S, Cioffi R, Montagnaro F, Pisciotta F, Santo L (2006) Simultaneous adsorption of chlorophenol and heavy metal ions on organophilic bentonite. Appl Clay Sci 31:126–133. https://doi.org/10.1016/j.clay.2005.09.004
- Baba A, Gunduz O (2010) Effect of alteration zones on water quality: a case study from Biga peninsula, Turkey. Arch Environ Contam Toxicol 58:499–513. https://doi.org/10.1007/s00244-009-9406-8
- Baba A, Save D, Gündüz O, Gürdal G, Bozcu M, Sülün S, Özcan HO, Hayran, H. İkiişik, L. Bakırcı (2009) Effect of mining activity on human health. TÜBİTAK Project, Türkiye Bilimsel ve Teknik Araştırma Kurumu (TÜBİTAK) Project No: ÇAYDAG-106Y041, Ankara (in Turkish)
- Balarak D, Jaafari J, Hassani G, Mahdavi Y, Tyagi I, Agarwal S, Gupta VK (2015) The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: isotherm, kinetic and thermodynamic studies. Colloids Interface Sci Commun 7:16–19. https://doi.org/10.1016/j.colcom.2015.11.004

- Bechard G (1993) Microbiological process for the treatment of acid mine drainage using cellulosic substrates. Ph.D. Thesis; Department of Biology; Carleton University
- Blodau C (2006) A review of acidity generation and consumption in acidic coal mine lakes and their watersheds. Sci Total Environ 369:307–332. https://doi.org/10.1016/j.scitoteny.2006.05.004
- Can C, Jianlong W (2008) Investigating the interaction mechanism between zinc and Saccharomyces cerevisiae using combined SEM-EDX and XAFS. Appl Microbiol Biotechnol 79:293–299. https://doi.org/10.1007/s00253-008-1415-4
- Chuang CL, Fan M, Xu M, Brown RC, Sung S, Saha B, Huang CP (2005) Adsorption of arsenic (V) by activated carbon prepared from oat hulls. Chemosphere 61(4):478–483. https://doi.org/10.1016/j.chemosphere.2005.03.012
- Demirbas E, Kobya M, Oncel S, Sencan S (2002) Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. Bioresour Technol 84(3):291–293. https://doi.org/10.1016/s0960-8524(02)00052-4
- Escudero C, Gabaldón C, Marzal P, Villaescusa I (2008) Effect of EDTA on divalent metal adsorption onto grape stalk and exhausted coffee wastes. J Hazard Mater 152:476–485. https://doi.org/10.1016/j.jhazmat.2007.07.013
- Evangelou VP (1998) Pyrite oxidation control. In: Geller W, Klapper H, Salomons W (eds) Acidic mining lakes—acid mine drainage", limnology and reclamation. Springer, Berlin, pp 419–421
- Farinella NV, Matos GD, Arruda MAZ (2007) Grape bagasse as a potential biosorbent of metals in effluent treatments. Bioresour Technol 98(10):1940–1946. https://doi.org/10.1016/j.biortech.2006.07.043
- Friese K, Hupfer M, Shultze M (1998) Chemical characteristics of water and sediment in acidic mining lakes of the Lusatian Lignite District. In: Geller W, Klapper H, Salomons W (eds) Acidic mining lakes—acid mine drainage, limnology and reclamation. Springer, Berlin, pp 25–45
- Gaballah I, Kilbertus G (1998) Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks. J Geochem Explor 62:241–286. https://doi.org/10.1016/s0375-6742(97)00068-x
- Gardea-Torresdey JL, Tang L, Salvador JM (1996) Copper adsorption by esterified and unesterified fractions of Sphagnum peat moss and its different humic substances. J Hazard Mater 48:191–206. https://doi.org/10.1016/0304-3894(95)00156-5
- Geller W, Klapper H, Schultze M (1998) Natural and anthropogenic sulfuric acidification of lakes. In: Geller W, Klapper H, Salomons W (eds) Acidic mining lakes—adic mine drainage, limnology and reclamation. Springer, Berlin, pp 3–14
- General Directorate of Mineral Research, Exploration (2002) Geological map of Turkey, scale 1:500.000. MTA, Ankara
- Gharaibeh SH, Abu-El-Sha'r WY, Al-Kofahi MM (1998) Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products. Water Res 32:498–502. https://doi.org/10.1016/s0043-1354(97)00221-2
- Gunduz O, Baba A (2008) Fate of acidic mining lakes in Can Lignite District, Turkey. In: Proceedings of the XXXVI IAH congress integrating groundwater science and human well-being proceedings CD-ROM., October, Toyama, Japan
- Gunduz O, Okumusoglu D, Baba A (2007) Acidic mining lakes and their influence on water quality: a case study from Can (Canakkale), Turkey. In: Proceedings of the 6th International groundwater quality conference GQ07: securing groundwater quality in urban and Industrial environments, Fremantle, Western Australia. ISBN: 978-0-643-095519
- Gupta VK, Saleh TA (2013) Sorption of pollutants by porous carbon, carbon nanotubes and fullerene—an overview. Environ Sci Pollut Res 20(5):2828–2843. https://doi.org/10.1007/s11356-013-1524-1





- Gupta VK, Srivastava SK, Mohan D, Sharma S (1998) Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions. Waste Manag 17(8):517–522. https://doi.org/10.1016/s0956-053x(97)10062-9
- Gupta VK, Rastogi A, Saini VK, Jain N (2006) Biosorption of copper(II) from aqueous solutions by *Spirogyra* species. J Colloid Interface Sci 296:59–63. https://doi.org/10.1016/j. icis.2005.08.033
- Gupta VK, Agarwal S, Saleh TA (2011) Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. J Hazard Mater 185(1):17–23. https://doi.org/10.1016/j.jhazmat.2010.08.053
- Gupta VK, Jain R, Mittal A, Saleh TA, Nayak A, Agarwal S, Sikarwar S (2012a) Photo-catalytic degradation of toxic dye amaranth on TiO₂/UV in aqueous suspensions. Mater Sci Eng, C 32(1):12–17. https://doi.org/10.1016/j.msec.2011.08.018
- Gupta VK, Ali I, Saleh TA, Nayak A, Agarwal S (2012b) Chemical treatment technologies for waste-water recycling—an overview. RSC Adv 2(16):6380–6388. https://doi.org/10.1039/c2ra20340e
- Gupta VK, Kumar R, Nayak A, Saleh TA, Barakat MA (2013) Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. Adv Colloid Interface Sci 193:24–34. https://doi.org/10.1016/j.cis.2013.03.003
- Hamza IA, Martincigh BS, Ngila JC, Nyamori VO (2013) Adsorption studies of aqueous Pb (II) onto a sugarcane bagasse/multi-walled carbon nanotube composite. Phys Chem Earth Parts A/B/C 66:157–166. https://doi.org/10.1016/j.pce.2013.08.006
- Hasan S, Hashim MA, Sen Gupta B (2000) Adsorption of Ni(SO₄) on Malaysian rubber-wood ash. Bioresour Technol 72:153–158. https://doi.org/10.1016/s0960-8524(99)00101-7
- Hegazi HA (2013) Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. HBRC J 9(3):276–282. https://doi.org/10.1016/j.hbrcj.2013.08.004
- Ilay R, Kavdir Y, Sümer A (2013) The effect of olive oil solid waste application on soil properties and growth of sunflower (*Helianthus annuus* L.) and bean (*Phaseolus vulgaris* L.). Int Biodeterior Biodegrad 85:254–259. https://doi.org/10.1016/j.ibiod.2013.07.008
- Iqwe JC, Ogunewe DN, Abia AA (2005) Competitive adsorption of Zn (II), Cd (II) and Pb(II) ions from aqueous and non-aqueous solution by maize cob and husk. Afr J Biotechnol 4(10):1113–1116
- Kadirvelu K, Thamaraiselvi K, Namasivayam C (2001) Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresour Technol 76(1):63–65. https://doi.org/10.1016/S0960 -8524(00)00072-9
- Kaikake K, Hoaki K, Sunada H et al (2007) Removal characteristics of metal ions using degreased coffee beans: adsorption equilibrium of cadmium(II). Bioresour Technol 98:2787–2791. https://doi. org/10.1016/j.biortech.2006.02.040
- Karakas G, Brookland I, Boehrer B (2003) Physical characteristics of acidic mining lake 111. Aquat Sci 65:297–307. https://doi. org/10.1007/s00027-003-0651-z
- Kelly-Vargas K, Cerro-Lopez M, Reyna-Tellez S, Bandala ER, Sanchez-Salas JL (2012) Biosorption of heavy metals in polluted water, using different waste fruit cortex. Phys Chem Earth Parts A/B/C 37:26–29. https://doi.org/10.1016/j.pce.2011.03.006
- Khan TA, Sharma S, Ali I (2011) Adsorption of Rhodamine B dye from aqueous solution onto acid activated mango (*Magnifera indica*) leaf powder: equilibrium, kinetic and thermodynamic studies. J Toxicol Environ Health Sci 3:286–297
- Kirsten W (1983) Organic elemental analysis: ultramicro, micro, and trace methods. Academic Press, Harcourt Brace Jovanovich, New York
- Kurniawan TA, Chan GY, Lo WH, Babel S (2006) Comparisons of lowcost adsorbents for treating wastewaters laden with heavy metals.

- Sci Total Environ 366(2):409–426. https://doi.org/10.1016/j.scito tenv.2005.10.001
- Lee SH, Jung CH, Chung H, Lee MY, Yang JW (1998) Removal of heavy metals from aqueous solution by apple residues. Process Biochem 33(2):205–211. https://doi.org/10.1016/s0032-9592(97)00055-1
- Lesage-Meessen L, Navarro D, Maunier S, Sigoillot JC, Lorquin J, Delattre M et al (2001) Simple phenolic content in olive oil residues as a function of extraction systems. Food Chem 75:501–507. https://doi.org/10.1016/s0308-8146(01)00227-8
- Liu R, Ma W, Jia CY, Wang L, Li HY (2007) Effect of pH on biosorption of boron onto cotton cellulose. Desalination 207(1–3):257–267. https://doi.org/10.1016/j.desal.2006.07.012
- López-Mesas M, Navarrete ER, Carrillo F, Palet C (2011) Bioseparation of Pb(II) and Cd (II) from aqueous solution using cork waste biomass. Modeling and optimization of the parameters of the biosorption step. Chem Eng J 174(1):9–17. https://doi.org/10.1016/j.cej.2011.07.026
- Malkoc E, Nuhoglu Y (2007) Potential of tea factory waste for chromium (VI) removal from aqueous solutions: thermodynamic and kinetic studies. Sep Purif Technol 54(3):291–298. https://doi.org/10.1016/j.seppur.2006.09.017
- Martinez M, Miralles N, Hidalgo S, Fiol N, Villaescusa I, Poch J (2006) Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste. J Hazard Mater 133:203–211. https://doi.org/10.1016/j.jhazmat.2005.10.030
- Martín-Lara MA, Pagnanelli F, Mainelli S, Calero M, Toro L (2008) Chemical treatment of olive pomace: effect on acid-basic properties and metal biosorption capacity. J Hazard Mater 156:448–457. https://doi.org/10.1016/j.jhazmat.2007.12.035
- MEND (1994) Canada-wide survey of acid mine drainage characteristics; Canada Center for Mineral and Energy Technology (CAN-MET); MEND Project 3.22.1
- Meunier N, Laroulandie J, Blais JF, Tyagi RD (2003) Cocoa shells for heavy metal removal from acidic solutions. Bioresour Technol 90:255–263. https://doi.org/10.1016/s0960-8524(03)00129-9
- Mittal A, Mittal J, Malviya A, Gupta VK (2009) Adsorptive removal of hazardous anionic dye "Congo red" from wastewater using waste materials and recovery by desorption. J Colloid Interface Sci 340(1):16–26. https://doi.org/10.1016/j.jcis.2009.08.019
- Mittal A, Mittal J, Malviya A, Gupta VK (2010) Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. J Colloid Interface Sci 344(2):497–507. https://doi.org/10.1016/j. jcis.2010.01.007
- Nadaroglu H, Kalkan E, Demir N (2010) Removal of copper from aqueous solution using red mud. Desalination 251:90–95. https://doi.org/10.1016/j.desal.2009.09.138
- Naiya TK, Bhattacharya AK, Mandal S, Das SK (2009) Adsorption of Zn(II), Cd(II) and Pb(II) onto fly ash. In: Shengcai L, Yajun W, Fengxia C, Ping H, Yao Z (eds) Progress in environmental science and technology, vol 2. Science Press, Monmouth Junction, pp 2041–2051
- Nasernejad B, Zadeh TE, Pour BB, Bygi ME, Zamani A (2005) Camparison for biosorption modeling of heavy metals (Cr(III), Cu (II), Zn (II)) adsorption from wastewater by carrot residues. Process Biochem 40:1319–1322. https://doi.org/10.1016/j.procb jo.2004.06.010
- Oztürk N, Kavak D (2005) Adsorption of boron from aqueous solutions using fly ash: batch and column studies. J Hazard Mater 127:81–88. https://doi.org/10.1016/j.jhazmat.2005.06.026
- Pagnanelli F, Mainelli S, Vegliò F, Toro L (2003) Heavy metal removal by olive pomace: biosorbent characterisation and equilibrium modelling. Chem Eng Sci 58(20):4709–4717. https://doi.org/10.1016/j.ces.2003.08.001



- Periasamy K, Namasivayam C (1996) Removal of copper(II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater. Chemosphere 32(4):769–789. https://doi.org/10.1016/0045-6535(95)00332-0
- Qi BC, Aldrich C (2008) Biosorption of heavy metals from aqueous solutions with tobacco dust. Bioresour Technol 99(13):5595–5601. https://doi.org/10.1016/j.biortech.2007.10.042
- Reddad Z, Gérente C, Andrès Y et al (2003) Cadmium and lead adsorption by a natural polysaccharide in MF membrane reactor: experimental analysis and modelling. Water Res 37:3983–3991. https://doi.org/10.1016/s0043-1354(03)00295-1
- Report 1.20.1. December. http://www.fs.usda.gov/Internet/FSE_DOCUMENTS/stelprdb5336546.pdf
- Saravanan R, Shankar H, Prakash T, Narayanan V, Stephen A (2011) ZnO/CdO composite nanorods for photocatalytic degradation of methylene blue under visible light. Mater Chem Phys 125(1):277– 280. https://doi.org/10.1016/j.matchemphys.2010.09.030
- Saravanan R, Gupta VK, Narayanan V, Stephen A (2013a) Comparative study on photocatalytic activity of ZnO prepared by different methods. J Mol Liq 181:133–141. https://doi.org/10.1016/j.molliq.2013.02.023
- Saravanan R, Thirumal E, Gupta VK, Narayanan V, Stephen A (2013b) The photocatalytic activity of ZnO prepared by simple thermal decomposition method at various temperatures. J Mol Liq 177:394–401. https://doi.org/10.1016/j.molliq.2012.10.018
- Saravanan R, Gracia F, Khan MM, Poornima V, Gupta VK, Narayanan V, Stephen A (2015) ZnO/CdO nanocomposites for textile effluent degradation and electrochemical detection. J Mol Liq 209:374–380. https://doi.org/10.1016/j.molliq.2015.05.040
- Saravanan R, Sacari E, Gracia F, Khan MM, Mosquera E, Gupta VK (2016) Conducting PANI stimulated ZnO system for visible light photocatalytic degradation of coloured dyes. J Mol Liq 221:1029– 1033. https://doi.org/10.1016/j.molliq.2016.06.074
- Schultze M, Geller W (1996) The acid lakes of lignite mining district of the former German Democratic Republic. In: Reuther R (ed) Geochemical approaches to environmental engineering of metals. Springer, Berlin; Heidelberg; New York, pp 89–105. ISBN 3-540-58848-5
- Sun G, Shi W (1998) Sunflower stalks as adsorbents for the removal of metal ions from wastewater. Ind Eng Chem Res 37:1324–1328. https://doi.org/10.1021/ie970468j
- TUİK (2015) Turkish Statistical Institute. http://www.tuik.gov.tr/PreIs tatistikTablo.do?istab_id=1073. Accesed 02 June 2016
- Veglio F, Beolchini F (1997) Removal of metals by biosorption: a review. Hydrometallurgy 44(3):301–316. https://doi.org/10.1016/ s0304-386x(96)00059-x
- Vijayaraghavan K, Palanivelu K, Velan M (2006) Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab

- shell particles. Bioresour Technol 97:1411–1419. https://doi.org/10.1016/j.biortech.2005.07.001
- Vile MA, Wieder RK (1993) Alkalinity generation by {Fe}({III}) reduction versus sulfate reduction in wetlands constructed for acid mine drainage treatment. Water Air Soil Pollut 69:425–441
- Villaescusa I, Fiol N, Martinez M et al (2004) Removal of cooper and nickel ions from aqueous solutions by grape stalks wastes. Water Res 38:992–1002
- Wang XS, Qin Y, Li Z-F (2006) Biosorption of zinc from aqueous solutions by rice bran: kinetics and equilibrium studies. Sep Sci Technol 41:747–756. https://doi.org/10.1080/01496390500527951
- Wang XS, Li ZZ, Tao SR (2009) Removal of chromium (VI) from aqueous solution using walnut hull. J Environ Manag 90:721–729. https://doi.org/10.1016/j.jenvman.2008.01.011
- Weng CH, Huang CP (2004) Adsorption characteristics of Zn(II) from dilute aqueous solution by fly ash. Colloids Surf A Physicochem Eng Asp 247:137–143. https://doi.org/10.1016/j.colsurfa.2004.08.050
- Wisotzky F, Obermann P (2001) Acid mine groundwater in lignite overburden dumps and its prevention—the Rhineland lignite mining area (Germany). Ecol Eng. https://doi.org/10.1016/s0925-8574(00)00152-x
- Wolf A, Watson M, Wolf N (2003) Digestion and dissolution methods for P, K, Ca, Mg and trace elements. In: Peters J (ed) Recommended methods of manure analysis, vol A3769. University of Wisconsin Extension Publication, Madison, pp 30, 32–35
- Yucel DS, Baba A (2013) Geochemical characterization of acid mine lakes in northwest turkey and their effect on the environment. Arch Environ Contam Toxicol 64:357–376. https://doi.org/10.1007/s00244-012-9843-7
- Yucel DS, Baba A (2016) Prediction of acid mine drainage generation potential of various lithologies using static tests: Etili coal mine (NW Turkey) as a case study. Environ Monit Assess 188:473. https://doi.org/10.1007/s10661-016-5462-5
- Yucel DS, Yucel MA, Baba A (2014) Change detection and visualization of acid mine lakes using time series satellite image data in geographic information systems (GIS): Can (Canakkale) County, NW Turkey. Environ Earth Sci. https://doi.org/10.1007/s1266 5-014-3330-6
- Yucel DS, Balcı N, Baba A (2016) Generation of acid mine lakes associated with abandoned coal mines in Northwest Turkey. Arch Environ Contam Toxicol 70:757–782. https://doi.org/10.1007/ s00244-016-0270-z.
- Zhou X, Korenaga T, Takahashi T, Moriwake T, Shinoda S (1993) A process monitoring/controlling system for the treatment of wastewater containing chromium (VI). Water Res 27:1049–1054. https://doi.org/10.1016/0043-1354(93)90069-t



