

Remediation of Wastewater Containing Heavy Metals Using Modified Diatomite

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Abstract: Diatomite, wood fly ash and their mixture with TiO_2 were tested as adsorption substrates for copper and cadmium cations removal from wastewater. Raw diatomite and wood ash were pretreated and stabilized by washing and were comparatively investigated as adsorption substrates for heavy metals. Further on, a composite mix of pretreated diatomite and wood ash was obtained by mixing with nano-structured TiO_2 , to increase the surface area of the substrate materials. The novel adsorbent was investigated in terms of crystallinity (XRD), surface properties (AFM, SEM, porosity and BET surface) and surface chemistry (EDX, FTIR). Equilibrium studies demonstrated that the novel material has a high capacity for Cu^{2+} and Cd^{2+} removal, showing removal efficiencies above 80% for cadmium and of 99% for copper cations, in optimised adsorption experiments. In this paper the kinetic mechanisms of the cation adsorption are discussed and are correlated with the substrates properties.

Keywords: Diatomite, adsorption, heavy metals, wastewater.

1. INTRODUCTION

Water is a limited resource. Over 40% of the world's population lives close to one of the 276 international watercourses but, due pollution and poor treatment, water is today increasingly at the centre of tensions and disputes between groups sharing water resources [1] as it cannot be re-used in agriculture or as drinking water source; thus, water remediation represents a term that currently describes the actions that might contribute to increase the water re-use, after various treatment processes [2].

Heavy metals represent a common and dangerous pollutant. Some industries such as mining, electroplating, ceramics, battery manufacturing are considered as main sources for heavy metals pollution. Discharged in the natural flows without (sufficient) treatment, the pollutants can reach concentrations up to some hundreds of mg/L causing economic problems (costly water treatment) and a variety of illnesses (respiratory problems, eczemas, cancer) [3].

Many treatment processes have been evaluated to remove heavy metals from wastewater: chemical precipitation, ion exchange [4], membrane (nano) filtration, reverse osmosis [5], activated carbon adsorption [6]. Among these, ion exchange, activated carbon adsorption and membrane filtration are highly efficient but are expensive. Still, adsorption technologies are considered to be particularly

competitive and effective for heavy metals removal even at traces level, down to the discharge limits and have several advantages, as being a mature technology: easy operation, common/inexpensive equipment, less sludge, adsorbents' reuse after desorption [7].

To fulfill the industrial requirements, low-cost adsorbents are intensively studied, mainly based on natural compounds (red mud [8], natural zeolites [9], bentonite [10], clay [11], and diatomite [12] moss peat [13]) or on wastes: bone char [14], activated sewage sludge [15], wood ash lime and fume dust [16].

Fly ash is another pollutant by-product, raising big environmental problems; the use of this waste as second raw material, in various applications becomes thus a sustainable solution [17, 18].

Diatomite is a natural material with a similar composition with wood or coal fly ash (SiO_2 53.32%, Al_2O_3 22.05, the minor constituents Fe_2O_3 8.97, Na_2O , K_2O , MgO , MnO , TiO_2) [19]. The main constituents of diatomite are silica (SiO_2) and aluminosilicates. The analysis shows that SiO_2 is the main component (above 70%) and the metal oxides (Al_2O_3 , Na_2O and Fe_2O_3) are the main minor constituents [20].

Diatomite is largely used in water purification, filtration of commercial fluids, clarification of juices, liquors and for the separation of various oils and chemicals [19]. Diatomite is a highly porous material with up to 80-90% voids index [21].

As a surface process, adsorption requires large specific surfaces and charged or highly polar surface

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components. Basically, any solid material with a microporous structure can be used as an adsorbent. Thus, combining diatomite with wood fly ash can form an efficient and low cost adsorbent with average large specific surface area. The addition of a third ionic compound, with nano-structured surface, can further improve the substrate quality, making it efficient in removing heavy metals at very low concentrations (hundreds of ppm), when diffusion tends to hinder adsorption.

Therefore, a new adsorbent material was obtained from diatomite, wood fly ash and TiO_2 . The structural and surface properties of the components in this adsorbent and of their mix are presented in this paper, along with their efficiency in removing two heavy metal cations, cadmium and copper.

2. EXPERIMENTAL

2.1. The Substrates

Three materials were mixed to obtain a new adsorbent material:

- 1) Wood fly ash, a waste resulted from burning fast growing biomass (energetic willow), collected from the Thermal Wood Power Station Miercurea Ciuc, Romania. The cost of wood fly ash is zero;
- 2) Diatomite natural material collected from the Brasov area, Romania;
- 3) TiO_2 Degussa P25 nano-powder, containing 20% rutile and 80% anatase, with the specific surface of about $50 \text{ m}^2/\text{g}$ and a grain size in average of 30nm.

The raw wood ash (100g) was washed with ultra-pure water (1000mL) under mechanical stirring (100 rpm, Nahita GJ-1 stirrer), at room temperature ($22 \pm 1^\circ\text{C}$), for 24h, to remove the soluble compounds. After 24h the suspension was filtered and dried at $105\text{--}115^\circ\text{C}$ overnight. The washed and dried wood ash (noted as WAw) was mechanically sieved and the fraction $20\text{--}40\mu\text{m}$ was selected.

The diatomite (100g) was modified (treated), by washing with ultra-pure water (1000mL) under mechanical stirring at room temperature ($22 \pm 1^\circ\text{C}$) for 24h and then was dried overnight; the washed diatomite is noted Dw. Diatomite is fine grained, and essentially consists of silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) [20, 21].

The TiO_2 nanopowder was used as received.

The individual WAw and Dw substrates and the three component material, obtained by mechanically mixing the three powders (WAw, Dw and TiO_2) were further investigated as substrates in heavy metals adsorption for the advanced wastewater treatment.

2.2. Substrates Characterization

The treated wood fly ash (WAw) and diatomite (Dw) crystalline structures were evaluated before adsorption by XRD (Advanced D8 Discover Bruker diffractometer, $\text{Cu}_{K\alpha 1} = 1.5406 \text{ \AA}$, 40kW, 20mA, 2θ range $10^\circ\text{--}70^\circ$, scanning step 0.02° , scan speed 2sec/step) and complementary data were obtained by FTIR spectroscopy (Spectrum BX Perkin Elmer BX II 75548, $\lambda = 400\text{--}4000 \text{ nm}$).

The surface characterization included porosity and BET specific surface measurements (Autosorb-IQ-MP, Quantachrome Instruments), morphology studies (roughness and particle size distribution) using AFM (Ntegra Spectra, NT-MDT model BL222RNTE, in semi-contact mode with Golden silicon cantilever, NCSG10, at constant force 0.15 N/m, with a 10nm tip radius) and scanning electron microscopy (SEM, S-3400N- Hitachi, accelerating voltage of 20 KV). Surface elemental composition was evaluated using energy dispersive X-ray spectroscopy (EDX, Thermo Scientific Ultra Dry).

2.3. Adsorption Tests

Batch adsorption experiments were done at room temperature ($18\text{--}22^\circ\text{C}$), under mechanical stirring. The mono-component systems were prepared using bidistilled water as solvent and the heavy metal cations from: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Scharlau Chemie S. A., $c < 98\%$) $c_i = 0\text{--}318 \text{ mg/L}$ or cadmium ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, Scharlau Chemie), $c_i = 0\text{--}600 \text{ mg/L}$.

The optimal contact time was evaluated using suspensions of 1 g substrate in 100 mL solution. Aliquots were taken at certain moments (15, 30, 45, 60, 90, 120, 180, 240 min), when stirring was briefly interrupted and after decantation and filtration the volumes of supernatant were analyzed.

The initial and the residual metal concentration in the aqueous solution was analysed by AAS (Analytic Jena, ZEE nit 700), at $\lambda_{\text{Cd}} = 228.8 \text{ nm}$ and at $\lambda_{\text{Cu}} = 324.75 \text{ nm}$.

The adsorption efficiency, η , and adsorption capacity, q_t , were evaluated based on eq. 3 and 4:

$$\eta = \frac{(c_{HM}^i - c_{HM}^t) \times 100}{c_{HM}^i} \quad (1)$$

$$q_t = \frac{(c_{HM}^i - c_{HM}^t) \times V}{m_s} \quad (2)$$

where c_{HM}^i and c_{HM}^t represent the initial and momentary Cd^{2+} , Cu^{2+} concentrations (mg/L), V the solution volume (L) and m_s is the amount of substrate (Dw, WAw, DWA-TiO₂, g).

3. RESULTS AND DISCUSSIONS

3.1. The Substrates

As part of their treatment, diatomite and wood ash were washed and the final pH and conductivity values of the supernatant are quite different, proving that these materials contain different amounts of soluble oxides (Na₂O, K₂O, lime etc.), exceedingly higher for the wood ash, as Table 1 shows. These values confirm that the wood ash has an increased content of strongly alkaline soluble compounds (sodium and potassium oxides), leading to much bigger pH values than diatomite, although the conductivity is similar. These results could also be correlated with the carbonation effect on the natural diatomite surface, with the formation of soluble compounds with lower alkalinity.

Table 1: The Conductivity and pH Values in the Washing Water of the Samples

Material	pH	Conductivity [mS/cm]
Wood Ash	12.2	17.96
Diatomite	10.5	18.22

The XRD spectra, Figures 1 and 2 show crystalline structures both for WAw and Dw, the major components being SiO₂ (quartz) combined with Al₂O₃, carbon (graphite), hematite (Fe₂O₃) and MnO₂. Phosphorous based compounds are also identified in WAw, as expected, considering the usual wood composition (with phosphorus amounting about 0.05%-w). This similar composition supports the good compatibility of a future WAw-Dw composite.

The composition of the crystalline phases of diatomite is: quartz syn (hexagonal) 52,17%, nepheline syn, Na AlSiO₄ (hexagonal) - 11,12%, sodium aluminium silicate, Na₂O-Al₂O₃-SiO₂ - 23,91%, jacobite syn, MnFe₂O₄ (cubic) - 5,31%, manganese oxide, Mn₃O₄ (cubic) - 7,49%.

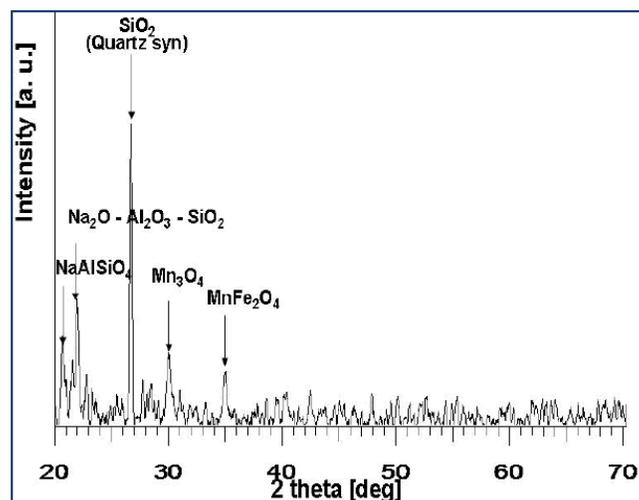


Figure 1: XRD patterns of Diatomite (Dw) substrate.

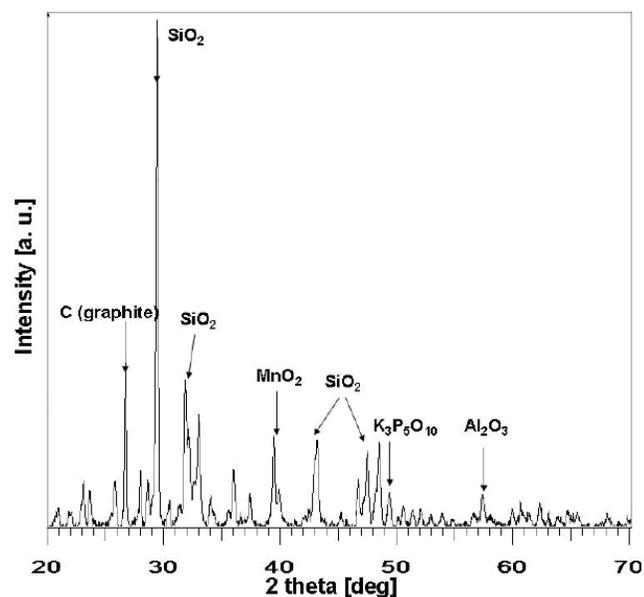


Figure 2: XRD patterns of wood ash (WAw) substrate.

The predominant oxide composition, generally recognized as having negatively charged surface due to the oxygen surface ions, represents an asset in cations adsorption.

Further on, morphology is investigated as large specific surface is a second pre-requisite for a good substrate. As the images in Figure 3 show, heterogeneous agglomerates are characterizing the materials and diatomite and wood ash grains are significantly larger (2.24....23,3µm) than the individual particles. The EDX, Table 2, data confirm the oxide composition; diatomite shows silica/silicate as main components and very low amounts of the other oxides, as result of the dissolutions during washing.

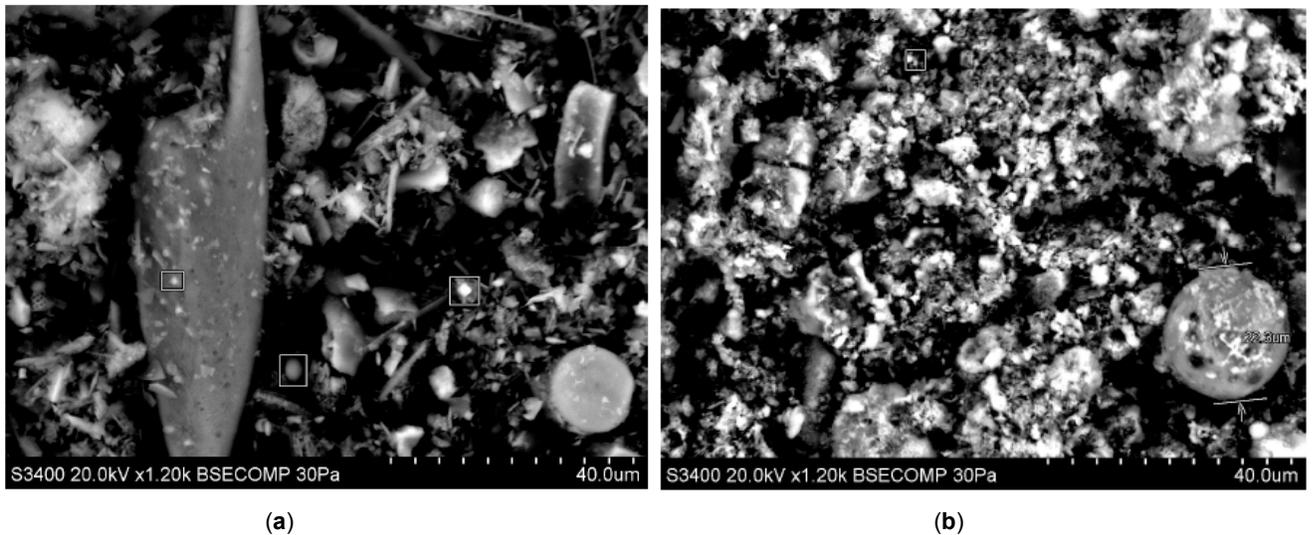


Figure 3: SEM images of (a) Diatomite and (b) Wood ash grains.

Table 2: Surface Elemental Composition of (a) Diatomite (Dw) and (b) Wood ash (WAw)

Element line (diatomite, Dw)	Atomic [%]	Element line Fly wood (WAw)	Atomic [%]
O K	70.02	O K	73.06
Na K	0.08	Na K	0.14
Al K	1.03	Mg K	2.15
Si K	28.02	Al K	0.16
K K	0.08	Si K	2.73
Ca K	0.06	P K	2.05
Ti K	0.05	K K	2.92
Fe K	0.37	Ca K	15.89

For the wood ash, the surface composition mainly consists of glassy compounds (hard to dissolve) and carbon or carbon-based compounds.

The FT-IR spectra of the materials were used to investigate the bands associated with the compounds, Figure 4 and Table 3. The results confirm the XRD and EDX findings, confirming the composition rich in carbonates in the wood ash and the silicates/aluminosilicates existent in both samples.

The washing process of diatomite and of WAw includes dissolution, recrystallization and new components development, [23]. The result is a rough surface, with RMS values above 200 nm (Figure 5b), suitable for adsorption as having a large amount of high energy active sites.

These AFM images were used to outline the surface morphology: the uniformity, grain size and pore size

distribution [24] of the samples and show, Figure 4, that the aggregates are assembled in grains, leaving wide open and regular pores on the surface (in the micrometric range for fly ash and about ten times lower for diatomite).

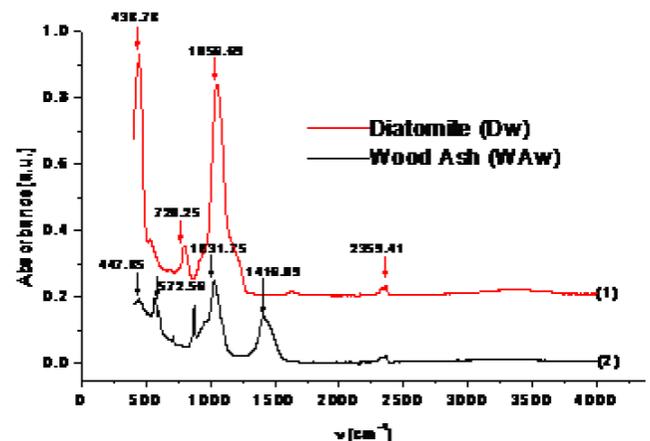
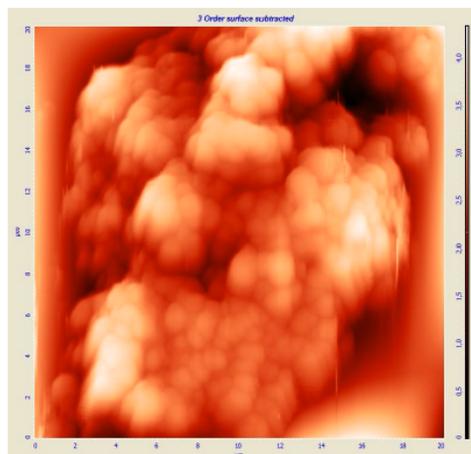


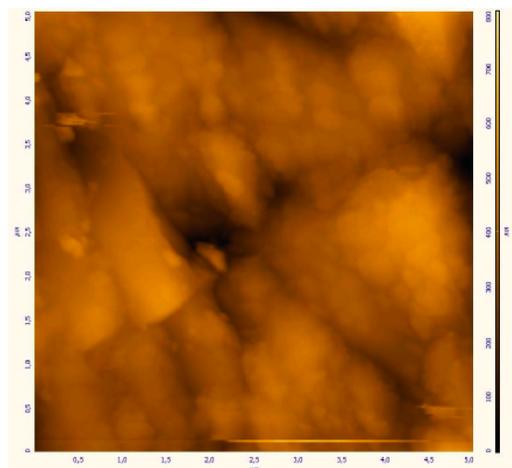
Figure 4: FTIR spectra of (1) diatomite and (2) wood ash.

Table 3: Characteristics of IR Bands Associated with Compounds [22]

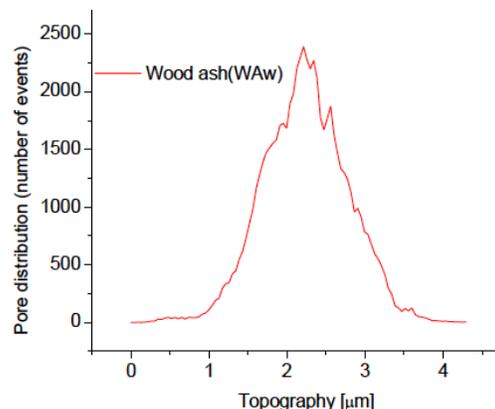
Type of IR band vibrational	Compounds	Frequency [cm ⁻¹]
C – O from CO ₃ ²⁻ alkaline	Materials free in air.	1410 – 1455
Asymmetric stretch of T – O bond	Quartz	1028...1150
Symmetric stretch of Si– O – Si bond	Caolin /Feldspats	720...770
T – O bending vibration	Caolin/hematite	570...590
Vibration in open pores,	Caolin/ zeolite	400...420



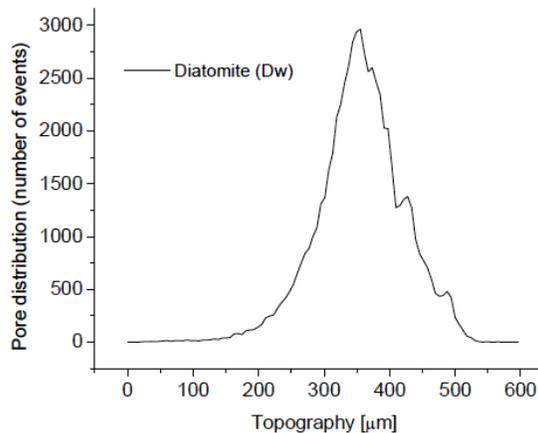
a) Wood ash; Roughness: 484.8 nm



b) Diatomite; Roughness: 210.7 nm



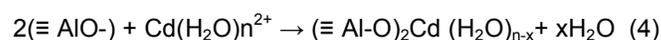
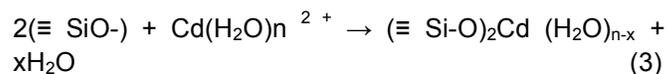
The interparticle voids distribution



The interparticle voids distribution

Figure 5: AFM topography, average roughness and macro-pore size distribution in: a) wood fly ash (WAw); b) Diatomite (Dw).

As both substrates are rich in silica and alumina, they can form alumino-silicates with different number of water molecules. These groups can develop new adsorption sites ($\equiv \text{SiO}^-$) and ($\equiv \text{AlO}$), increasing the negative surface charge and allowing the Cu^{2+} and Cd^{2+} cations to form new complexes at the surface of substrates [25]:



The specific surface area of the ash samples was measured by BET-method and the results are presented in Table 4:

Table 4: BET Area and Porosity Measurements for the Ash Substrates

Ash Sample	BET-Area [m ² /g]	Micropores Volume [cm ³ /g]	Micropores surface [m ² /g]	Average pores diameter [nm]
D	10.95	0.000807	4.07	25.59
WA	14.74	0.000367	4.45	17.32

These values confirm a nano-porous basic structure of the unit grains for both substrates and a rather high specific surface, with pores large enough to accommodate hydrated copper ($r = 0.295$ nm) or cadmium cations ($r = 0.426$ nm).

3.2. Heavy Metals Adsorption

The effect of the contact time on the efficiency of the Cd²⁺ and Cu²⁺ adsorption is presented in Figure 6.

The results show that the adsorption efficiency on diatomite is low and this can be a combined effect of the lower surface charge (as shown by the equilibrium pH) and lower specific surface. On the opposite, the results show the much higher affinity of both metal cations for wood ash, with higher negative surface charge (pH=12.2) and larger specific surface. It is also to notice the good results obtained for the copper cation adsorption, and this is the result of the higher mobility of this cation, with significantly lower hydration radius, [24].

To increase the specific surface and the oxide composition, the WAw + Dw combined powder was mixed with the highly water-stable TiO₂ Degussa P25;

previous investigations on coal fly ash (FAw) – TiO₂ mixtures outlined the optimal ratio FAw: TiO₂ = 3: 1 [25]. In the current experiments the ratio Dw : WAw : TiO₂ was set at 1:1:1. Two sets of experiments were done for each cation, using an initial amount of composite substrate (Dw + WAw + TiO₂ = 0.75g) and a doubled amount (2Dw + 2WAw + 2TiO₂ = 1.5g). The results obtained in optimized conditions showed moderate increase in the cadmium adsorption (up to 84%) and a strong increase of copper adsorption, up to 99%, Figure 7. This proves once again the significant role of the small nano-pores, corroborated with the actual size of the adsorbed specie, that influences the ionic strength and hydrated ionic radius (copper 0.295nm < cadmium 0.426nm).

The amount of adsorbent proving the highest efficiency was further used in kinetic investigations.

3.3. Uptake Kinetics of the Heavy Metals

Different kinetic adsorption mechanisms were tested (pseudo-first order, interparticle diffusion) but only the pseudo-second order kinetics, developed by Ho and McKay, [26], could well model the processes:

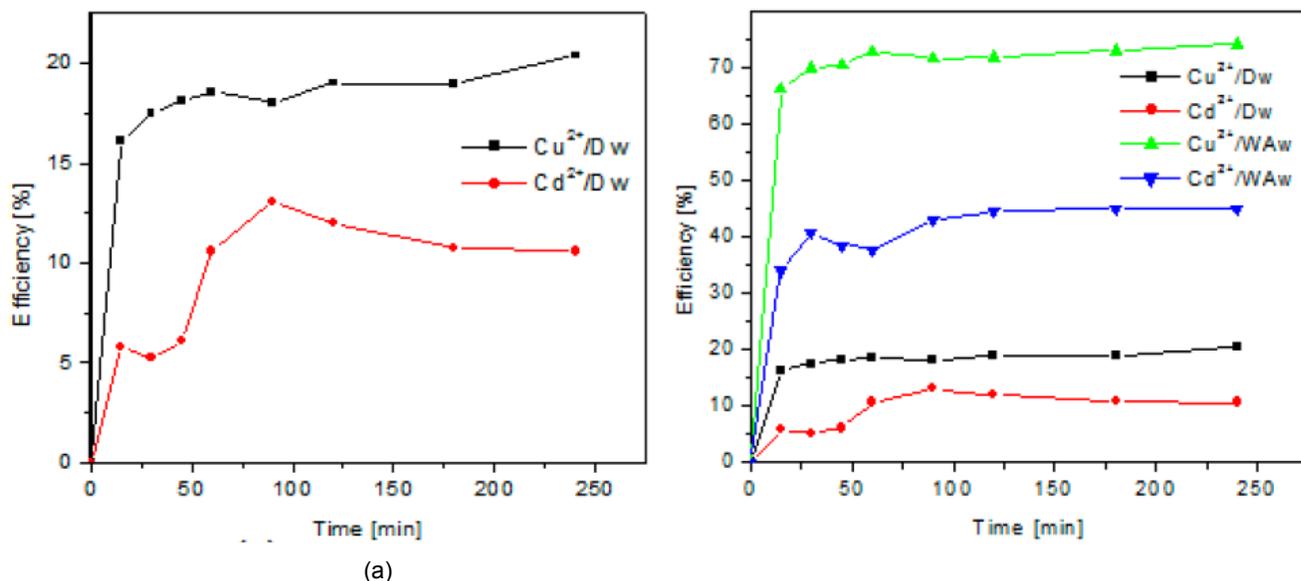


Figure 6: Influence of the contact time on the adsorption efficiency of Cd²⁺ and Cu²⁺ (a) on washed diatomite (Dw); (b) comparative adsorption efficiency on washed diatomite and on washed wood ash (WAw).

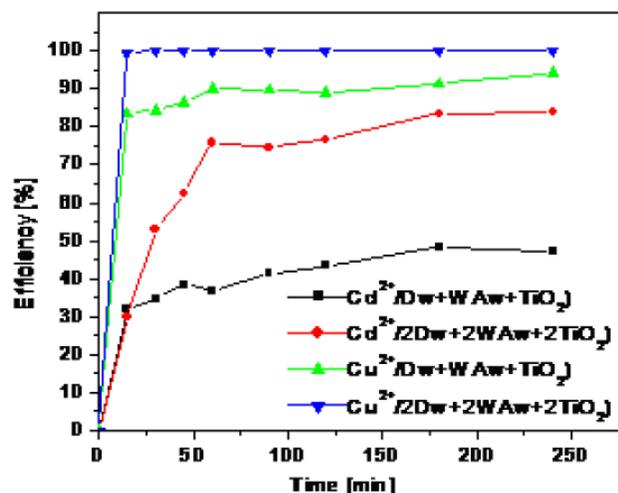


Figure 7: Time influence on the adsorption efficiency from Cd^{2+} and Cu^{2+} on the three- components substrate.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Table 5: Parameters of the Pseudo-Second Order Kinetics for Copper and Cadmium Adsorption

Parameter	Cd^{2+}		Cu^{2+}		Cd^{2+}	Cu^{2+}
	Dw	WAw	Dw	WAw	Dw+WAw+TiO ₂	Dw+WAw+TiO ₂
q_e [mg/g]	9.329	20.964	9.268	13.2	49.51	54.95
k_2 [g/mg min]	1.157	$6 \cdot 10^{-5}$	0.721	0.247	0.382	0.401
R^2	0.979	1.000	0.997	0.996	0.997	0.981

where k_2 is the pseudo second-order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), q_e and q_t are the amount of Cd^{2+}/MB ions adsorbed per unit mass of adsorbent (mg/g) at the equilibrium and at the current measurement moment t , respectively.

The kinetic parameters are presented in Table 5 for cadmium and copper removal.

The results confirm the larger adsorption capacity of the novel mixed substrate (WAw + Dw + TiO_2), both for copper and cadmium. This values show the real potential of the concept hereby exploited, of mixing nano-sized, nanostructured powders with mezzo- or micro-sized grains of wastes or natural materials.

The results also show that this capacity is mainly linked to the very small pores, more difficult to access, thus leading to slower kinetics. The fastest process is observed – as expected for the adsorption of the small and mobile copper cation.

4. CONCLUSIONS

A natural material (diatomite) and a waste (wood ash) proved to be effective adsorbents for heavy metals. Preliminary long duration treatment by washing is required, as the substrates are firstly releasing soluble alkaline compounds. The solubilization / reprecipitation processes during washing lead to surfaces with broad open pores and an increased amount of active sites.

By adding a nano-sized, nanostructure powder of a stable metal oxide, TiO_2 , leads to a three-component composite material, with much better adsorption capacity and efficiency, up to 99% for copper, in optimized conditions. The adsorption efficiency on this substrate also depends on the hydrated cation size, reaching 80% for cadmium, in optimized conditions.

The pseudo-second order kinetic applied to both heavy metals cations (Cd^{2+} and Cu^{2+}) shows a faster copper adsorption.

These data indicate that this mixture represents a sustainable, low cost solution for the remediation of industrial wastewaters loaded with heavy metals, as being able to efficiently remove the heavy metals even at low concentrations.

REFERENCES

- [1] Janssen F. Water for Life and Peace Ambassador, Green Cross 2012.
- [2] Thatai S, Khurana P, Boken J, Prasad S, Kumar D. Nanoparticles and core-shell nanocomposite based new generation water remediation materials and analytical techniques. A Review, *Microchem J* 2014; 116: 62-76. <http://dx.doi.org/10.1016/j.microc.2014.04.001>
- [3] Kabir Md. I, Daly E, Maggi F. A review of ion and metal pollutants in urban green water infrastructures. *Sci Total Environ* 2014; 470-71: 695-706.
- [4] Inglezakis VJ, Poupoulos SG. Adsorption, Ion Exchange and Catalysis. Elsevier, Amsterdam, Olanda 2006.
- [5] Ujang Z, Anderson GK. Performance of low pressure reverse osmosis membrane (LPROM) for separating mono- and divalent ions. *J Water Sci Technol* 1998; 38: 521. [http://dx.doi.org/10.1016/S0273-1223\(98\)00553-8](http://dx.doi.org/10.1016/S0273-1223(98)00553-8)

- [6] Sekar M, Sakthi V, Rengaraj S. Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *J Colloid Inter Sci* 2004; 279(2): 307-13.
- [7] Douglas Ruthven M. Principles of adsorption & Adsorption processes. Wiley-Interscience publication, New York 1984; ISBN 0-471-86606-7.
- [8] Çoruh S, Ergun ON. Copper Adsorption from Aqueous Solutions by Using Red Mud - An Aluminium Industry Waste. *Survival Sustainability Environ Earth Sci* 2011; 1275-1282.
- [9] Perić J, Trgo M, Medvidović NV. Removal of zinc, copper and lead by natural zeolite - a comparison of adsorption isotherms. *Water Res* 2004; 38: 1893-99. <http://dx.doi.org/10.1016/j.watres.2003.12.035>
- [10] Viša M. Tailoring fly ash activated with bentonite as adsorbent for complex wastewater treatment. *J Appl Surf Sci* 2012; 263: 753-62. <http://dx.doi.org/10.1016/j.apsusc.2012.09.156>
- [11] Anirudhan TS, Ramachandran M. Adsorption removal of tannin from aqueous solutions by cationic surfactant - modified bentonite clay. *J Colloid Inter Sci* 2006; 299: 116-24. <http://dx.doi.org/10.1016/j.jcis.2006.01.056>
- [12] Khraisheh MAM, Al-Degs YS, Mcminn WAM. Remediation of wastewater containing heavy metals using raw and modified diatomite. *Chem Eng J* 2004; 99: 177-84. <http://dx.doi.org/10.1016/j.cej.2003.11.029>
- [13] Balan C, Bulai P, Bilba D, Macoveanu M. Sphagnum moss peat: a green and economical sorbent for removal of heavy metals (Cd and Cr) from wastewaters. *Environ Eng Manag J* 2010; 9: 469-78.
- [14] Cheung CW, Porter JF, McKay G. Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char. *Water Res* 2000; 35: 605-12. [http://dx.doi.org/10.1016/S0043-1354\(00\)00306-7](http://dx.doi.org/10.1016/S0043-1354(00)00306-7)
- [15] Otero M, Rozzada F, Calvo LF, Garcia AI, Morán A. Elimination of organic water pollutant using adsorbents obtained from sewage sludge. *J Dyes Pigment* 2003b; 57: 55-56. [http://dx.doi.org/10.1016/S0143-7208\(03\)00005-6](http://dx.doi.org/10.1016/S0143-7208(03)00005-6)
- [16] Chirenje T, Ma LQ, Lu L. Retention of Cd, Cu, Pb and Zn by wood ash, lime and fume dust. *Water Air Soil Poll* 2006; 171: 301-14. <http://dx.doi.org/10.1007/s11270-005-9051-4>
- [17] Ahmaruzzaman M. A review on the utilization of fly ash. *Progr Energy Comb Sci* 2010; 36: 327-63. <http://dx.doi.org/10.1016/j.pecs.2009.11.003>
- [18] Viša M, Nacu M. Comparative heavy metals and dyes removal efficiency on fly ash and wood ash. *Environ Eng Manag J* 2011; 10(9): 1407-14.
- [19] Korunic Z. Diatomaceous earths, a group of natural insecticides. *J Stored Products Res* 1998; 34: 87-97. [http://dx.doi.org/10.1016/S0022-474X\(97\)00039-8](http://dx.doi.org/10.1016/S0022-474X(97)00039-8)
- [20] Loganina VI, Simonov EE, Jezierski W, Małaszkiwicz D. Application of activated diatomite for dry lime mixes. *Construct Building Mater* 2014; 65: 29-37. <http://dx.doi.org/10.1016/j.conbuildmat.2014.04.098>
- [21] Šljivić M, Smičiklas I, Pejanović S, Plečaš I. Comparative study of Cu²⁺ adsorption on a zeolite, clay and a diatomite from Serbia. *J App Clay Sci* 2009; 43: 33-40. <http://dx.doi.org/10.1016/j.clay.2008.07.009>
- [22] Chirenje T, Ma LQ, Lu L. Retention of Cd, Cu, Pb and Zn by wood ash, lime and fume dust. *Water Air Soil Poll* 2006; 171: 301-14. <http://dx.doi.org/10.1007/s11270-005-9051-4>
- [23] Visa M, Duta A. Advanced Cd²⁺ Removal On Dispersed TiO₂-Fly Ash. *Environ Eng Manag J* 7(4): 373-78.
- [24] Visa M, Isac I, Duta A. Fly ash adsorbents for multi-cation wastewater treatment.
- [25] Visa M, Duta A, Adsorption behavior of Cadmium and Copper compounds on mixture FA:TiO₂. *J Rev Roum Chim* 2010; 55: 167-73.
- [26] Ho YS, McKay G. Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods. *Water Res* 2006; 40: 119-25. <http://dx.doi.org/10.1016/j.watres.2005.10.040>