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COPPER REMOVAL ON WOOD–FLY ASH SUBSTRATES – THERMODYNAMIC STUDY

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For copper removal from aqueous solution by sawdust wood–fly ash substrates we tested three types of sawdust: oak wood, white poplar and willow mixing with fly ash. Pre-treatment processes were previously developed and optimized, to enhance the sawdust and the fly ash affinity for heavy metals adsorption. Efficiency removal of 98% on willow sawdust, 99% on white poplar and oak sawdust were obtained on substrates of wood–fly ash washed with distilled water. When the fly ash was washed with NaOH 2n, the efficiency removal dropped down to 30% on willow and to 48% on white poplar. The adsorption mechanism was investigated; the results indicate that the adsorptive behavior Cu^{2+} on sawdust wood–fly ash washed with distilled water satisfies the Langmuir assumption and the adsorption of the sawdust fly ash treated with NaOH is less efficient and could be modeled by the Freundlich equation.

INTRODUCTION

Heavy metals are common pollutants, resulting from industrial processing and plenty of research is dedicated to developing up-scalable, low-cost solutions. Diverse technologies have been used to reduce the contents of heavy metals in water. Adsorption methods using biosorbents have been widely noticed. In biosorption, studies have been tested various type of biomasses,[1] and/or different species belonging to a single type of biomass.[2-4]

Wood has cellulose and its derivatives as main components, therefore polar surfaces are expected, with affinity for polar and ionic pollutants, including heavy metals. Wood waste results in large quantities from the wood manufacturing and represents a slowly bio-degradable material, raising environmental problems. Single or combined with other waste material, wood can represent a low-cost alternative to the traditional substrates used in wastewater treatment (activated carbon, ion exchangers, zeolites). The use of wood wastes as second raw materials for developing novel adsorption substrates is thus a sustainable process, offering solutions for advanced wastewater treatment and for the use of wastes.[4,5]

Fly ash is a waste that also results in large amounts, mainly from combined heat and power plants. As such, fly ash is a mixture of crystalline oxides (SiO_2, CaO, K_2O, etc.) and unburned carbon and proved to be highly efficient in heavy metal removal from industrial wastewater, even at very low concentrations. Fly ash alone or mixed with TiO_2 proved to be efficient in heavy metal removal and photocatalytic degradation of dyes.[6-8]

Mixed substrates prove to exhibit synergy, therefore this paper reports on the adsorption efficiency in copper removal for substrates containing various types of wood and fly ash.

EXPERIMENTAL

Materials

Three types of sawdust are obtained from oak wood, (Querqus robur), white poplar, (Populus alba) and willow (Salix alba L.), collected from factories in the Dîmboviţa and Dolj regions. Before use, the sawdust is dried, in open atmosphere, at the room temperature (22 °C), for two weeks.

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Fly ash, FA, was collected from the electro-filter of the Braşov CPH/2009 plant from Roumania. The main components are SiO_2 (53%), Al_2O_3 (22%) and Fe_2O_3 (9%), therefore according to the ASTM standards it is of type F, thus it does not aggregate without lime addition. The minority components are alkaline and alkaline terrous oxides, along with titania, manganese oxides and unburned carbon.

Distilled water was used to prepare the solutions used in experiments: NaOH 2n (NaOH g.r., Lach-Ner, Czech Republic); Copper, standards, for AAS calibration (by diluting the stock solutions 1000 mg/L ions, Merck); $CuCl_2$, 3.12 10^{-4} – 10^{-2} mol/L ($CuCl_2 \cdot 2\,H_2O$ Merck).

Methods

1. Pre-treatment and analysis for substrates

The sawdust was treated with NaOH 3 mol/L, for 60 minute for oak sawdust and for 30 minute for willow and white poplar sawdust. The sawdust was further filtered, washed thoroughly with distillated water and dried at 105°C in oven. The sawdust: modifier (NaOH or water) ratio was set at 1:100 (g/mL), at 22°C.[4,5]

The fly ash was treated with distillated water for 48 hours (FA-W). Samples were further treated with NaOH 2n for 48 hours (FA-A). Afterwards, in a both cases, fly ash was filtered, washed with distillated water and dried at 105°C in oven. The ratio fly ash: distillated water or NaOH 2n was 1: 100 (g/ml), at 22°C.[7]

The sawdust structure and the FA crystalline structure ash was analyzed by XRD (Bruker D8 Discover Advanced Diffractometer) using the locked–couple technique, with 0.002 degree scan step and 0.01 seconds/step.

2. Analysis of the Cu (II) ions adsorption

The initial and residual metal ion concentration was determined, using an atomic absorption spectrophotometer, Perkin-Elmer AAS 400, with air-acetylene flame. The wavelength used in analysis corresponds to copper and was: λ_{Cu} = 324.74 nm.

The optimum sawdust-fly ash ratio was determined based on the correlation: adsorption efficiency vs. sawdust–fly ash ratio.

The efficiency was calculated on the initial c_M^i and momentary c_M^t concentrations of the metal (M):

$$\eta = \frac{(c_M^i - c_M^t)\times 100}{c_M^i} \qquad (1)$$

For the thermodynamic studies, adsorption experiments were developed on solutions in the concentrations range of 0.000312m…0.01m. The adsorption mechanism was investigated based on Langmuir and Freundlich isotherm models:

Langmuir model: $$\Gamma = \Gamma_{\max} \cdot \frac{ac_M^e}{1 + ac_M^e} \qquad (2)$$

Freundlich equation: $$\Gamma = kc_M^{e\;1/n} \qquad (3)$$

where: Γ represents the adsorption coefficient, Γ_{max} the maximum adsorption coefficient, a – the Langmuir parameter, k and n the Freundlich parameters. The data were refined based on the equilibrium concentration c_M^e, corresponding to the optimized adsorption duration.

RESULTS AND DISCUSSION

1. The adsorption substrates

The XRD patterns of untreated (natural) sawdust and for sawdust treated with NaOH 3mol/L are shown in Fig.1a and the XRD pattern of washed and modified FA are shown in Fig. 1b. The percentage of crystalline phase in the wood sawdust is presented in Table 1.

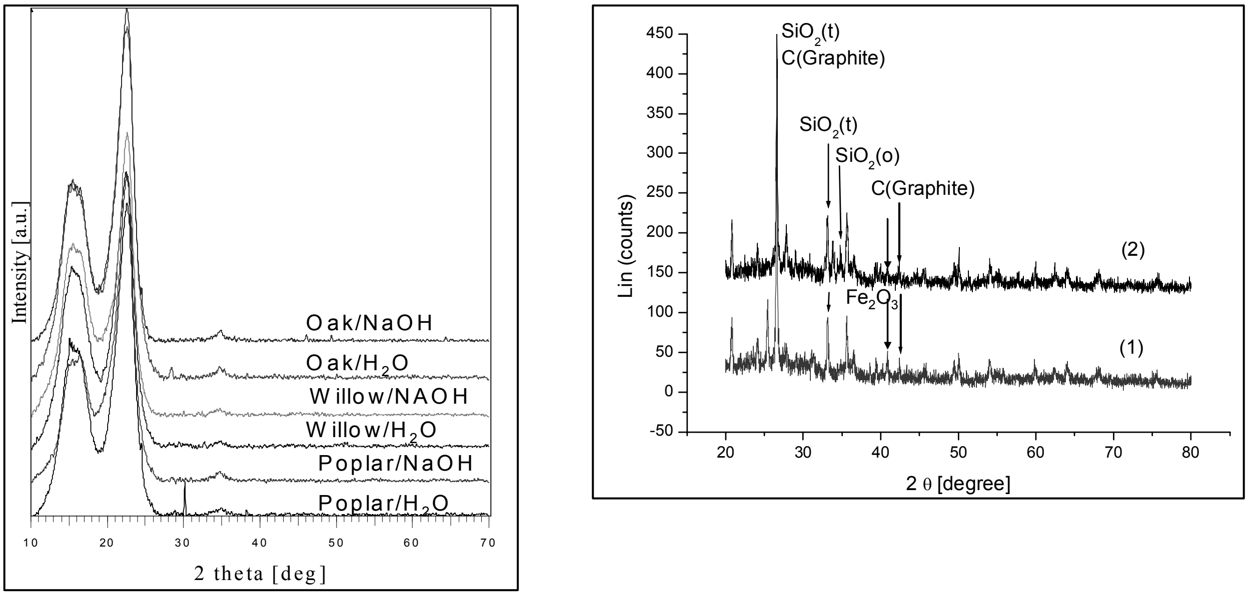
The data show that the wood substrates have a significant amount of crystalline phase, important for further adsorption and that for the porous structures (willow and poplar) the alkaline treatment reduces this phase, probably by “washing out” in chemical dissolution the inorganic compounds. This is confirmed by a set of small peaks that are no longer part of the XRD (corresponding to 2θ= 28.9; 37.2; 54.3). The more dense structure of oak hinders the dissolution processes and the increase of the crystalline phase can be correlated with partial crystallisation of the ions in environment, including NaOH. The XRD patterns for the raw and for modified fly ash confirm a poly–crystalline structure. The major components, quartz and graphite, are not affected during FA modification.

The surface characteristics for FA are presented in Table 2.[8]

Table 1

Crystalline of untreated and treatment sawdust

Sample	Crystalline phase [%]
White poplar natural	53.11
White poplar treatment with NaOH 3N solution	48.09
Willow natural	49.22
Willow treatment with NaOH 3N solution	44.41
Oak natural	47
Oak treatment with NaOH 3N solution	60.31



(a) (b)

Fig. 1 – XRD diffraction patterns for wood (a) and fly ash (b).

Table 2

Surface properties of FA

Component	BET surface area [m^2/g]	Total pore volume [cm^3/g]	Average pore diameter [nm]
FA	11.33	0.06	20.33

2. Optimizing the sawdust: fly ash ratio

Previous experiments,[5] showed the optimum adsorption time – at equilibrium corresponds to 60 minutes for oak, 30 minutes for willow and 15 minutes for white poplar, while the amount of substrate for 100mL of pollutant solution also depends on the wood type: for oak: 12g; for willow and white poplar: 8g. These values were further used in this study. The sawdust: fly ash ratio was varied as presented in Table 3.

Previous experimental tests were done on single component substrates (wood or fly ash) and the results proved that in both situations the alkali treatment increased the adsorption efficiency, up to 90% for fly ash,[6] and up to 90% for oak and poplar saw dust, at very low copper concentrations. [5]

At higher concentrations (over 0.03mol/L) fly ash preserved the adsorption affinity while the copper removal efficiency strongly decreased. Therefore, mixing the substrates was tested as a solution for quality enhancement of the sawdust as adsorbent, giving a new application for this waste.

The single substrates showed high affinity for copper after modifying them by 48h mixing with NaOH 3mol/L. Therefore, the first tests were done using mixed, alkali modified substrates, on Cu^{2+} solutions average concentrated (0.01 mol/L) and the results are presented in Fig. 2.

Table 3

Composition of the mixed substrates

Sample No.	Substrate 1		Substrate 2		Substrate 3	
	Oak (g)	FA (g)	Willow (g)	FA (g)	Poplar (g)	FA (g)
1	12	0	8	0	8	0
2	9	3	6	2	6	2
3	6	6	4	4	4	4
4	3	9	2	6	2	6
5	0	12	0	8	0	8

The results proved that good adsorption efficiencies are obtained on poplar mixed with FA (3:1). For the other two wood species efficiencies were below 90%, and the copper removal below the discharge limit (2mg/g) could not be reached in one single step adsorption. One reason for this behavior could be the pH value (two alkaline) that can lead to copper ion (partial) hydration, thus making adsorption more difficult.

Therefore, further investigations were done, on similarly concentrated copper solutions, by using modified wood sawdust and FA washed with distilled water. The results are presented in Fig. 3.

The best results were obtained on sawdust: FA-W mixtures with a 1:1 weight ratio, and the best wood substrate is oak (97%).

To elucidate these behaviour further investigations were done on the solutions pH, Table 4.

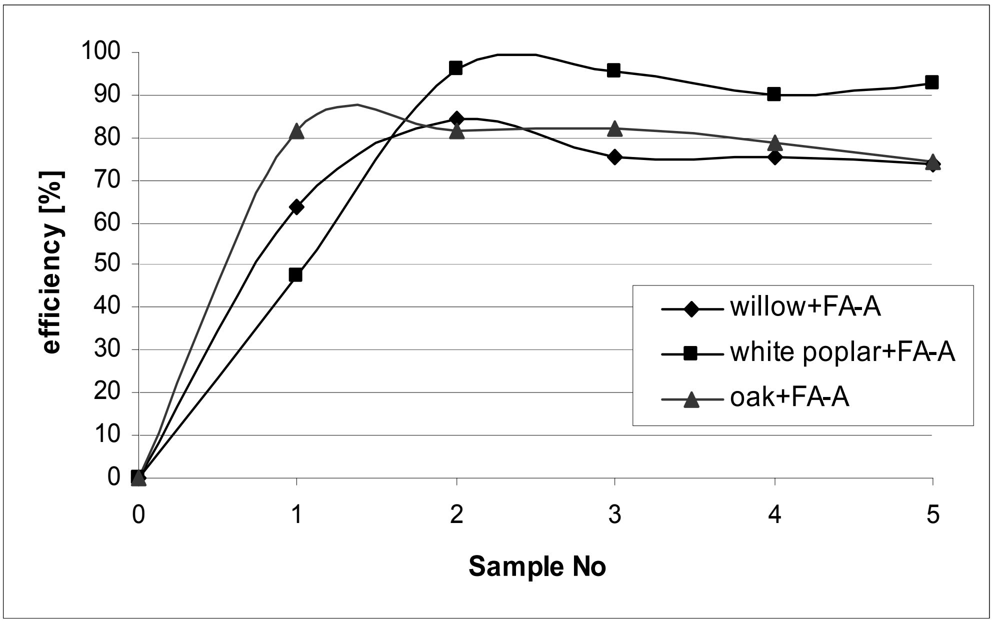


Fig. 2 – Effect of the ratio sawdust: alkali modified fly ash on Cu (II) sorption.

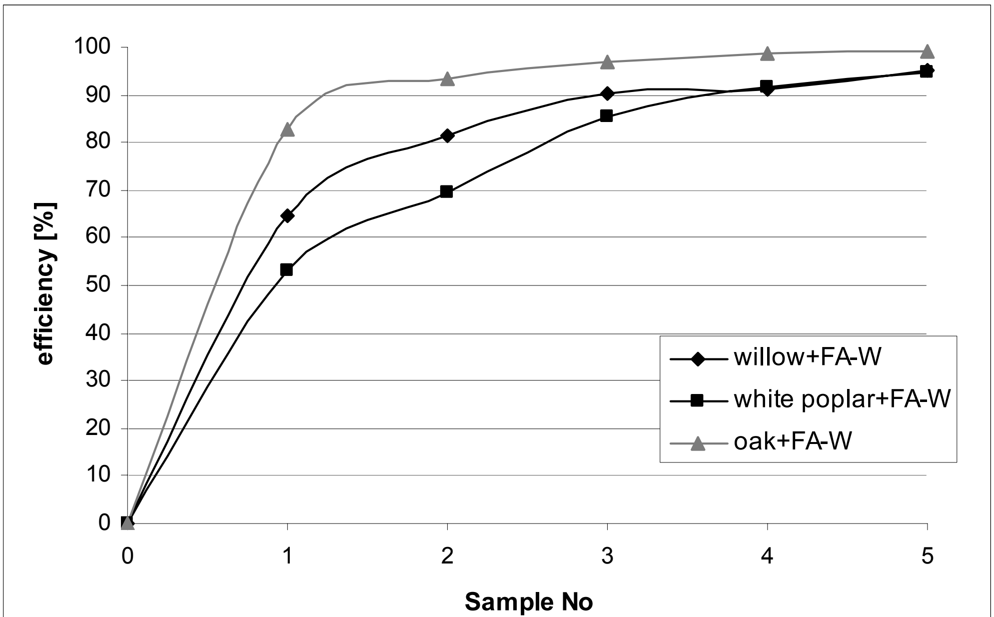


Fig. 3 – Effect of the ratio sawdust: fly ash washed with distillated on Cu(II) sorption.

Table 4

pH Values of the solutions at the adsorption equilibrium

Substrate types	$pH_{innitial}$	$pH_{adsoprtion}$
White poplar + FA-W		4.55
Willow + FA-W		4.48
Oak + FA-W		4.78
White poplar + FA-A	4.85	7.02
Willow + FA-A		7.08
Oak + FA-A		9.27
Fly Ash		7.8

The pH values indicate that in mixtures with FA-W, there is a slow acidification process, probably as result of slow NaOH desorption from the wooden substrate that induces low level coagulation of copper non-soluble compounds. Copper hydroxide full precipitation occurs at pH = 8.1, but Cu_2O formation starts at pH values close to 4.5. This could explain the decrease in the adsorption efficiencies, presented in Fig. 2, when the amount of alkaline treated FA increases. It is also important to consider the wood structures, light for poplar and willow and dense for oak. Oak alkali treated can accommodate crystalline NaOH that in the copper solution may re-dissolve. Further investigations are needed to elucidate the results involving oak. The slow and reversible adsorption of NaOH may not recommend alkali treated oak as adsorption substrate.

Based on these preliminary tests, and also considering the target of a low-cost adsorbent, further investigations were done on systems of wood sawdust mixed with FA-W, in a 1:1 ratio.

3. Effect copper (II) ion concentration

For determining the sorption capacity of a biosorbent, equilibrium sorption data are necessary at various metal initial concentrations. These data are further necessary for modeling adsorption isotherms. The results are presented in Fig. 4 and Fig. 5.

On the optimized substrates using FA-W, high efficiencies, above 96%, were obtained at concentrations up to 0.006mol/L. Similar tests were done on the mixed substrates with FA-A and the results are presented in Fig. 5.

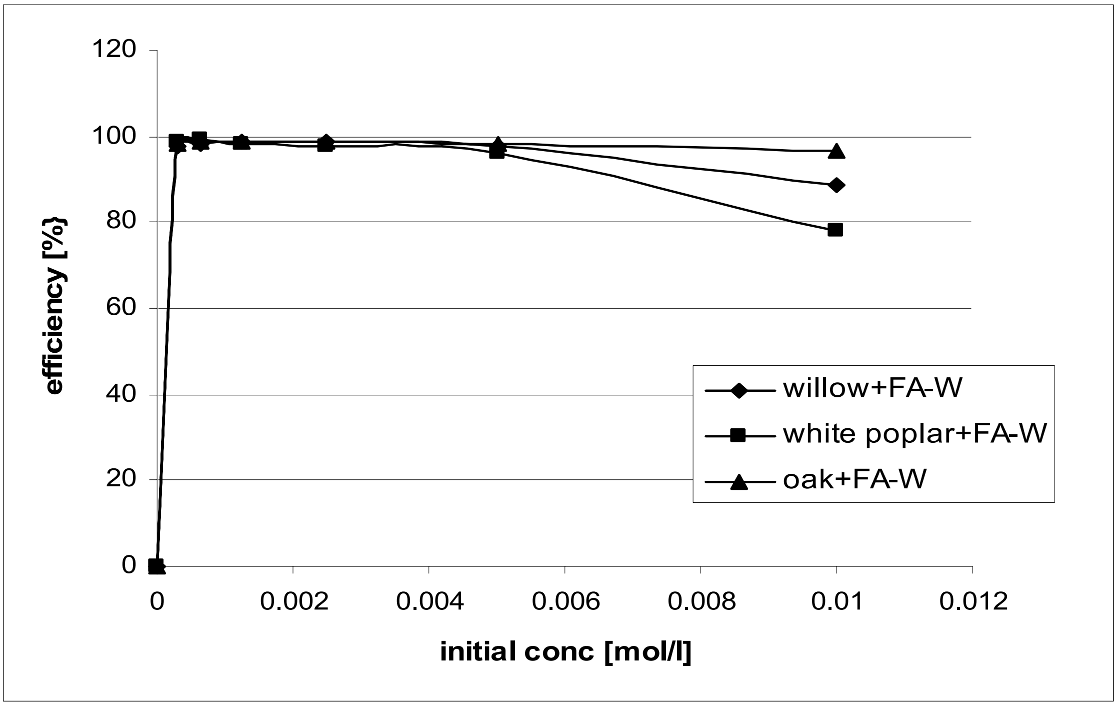


Fig. 4 – Influence of Cu(II) concentration on the adsorption efficiency on Sawdust: FA-W = 1:1.

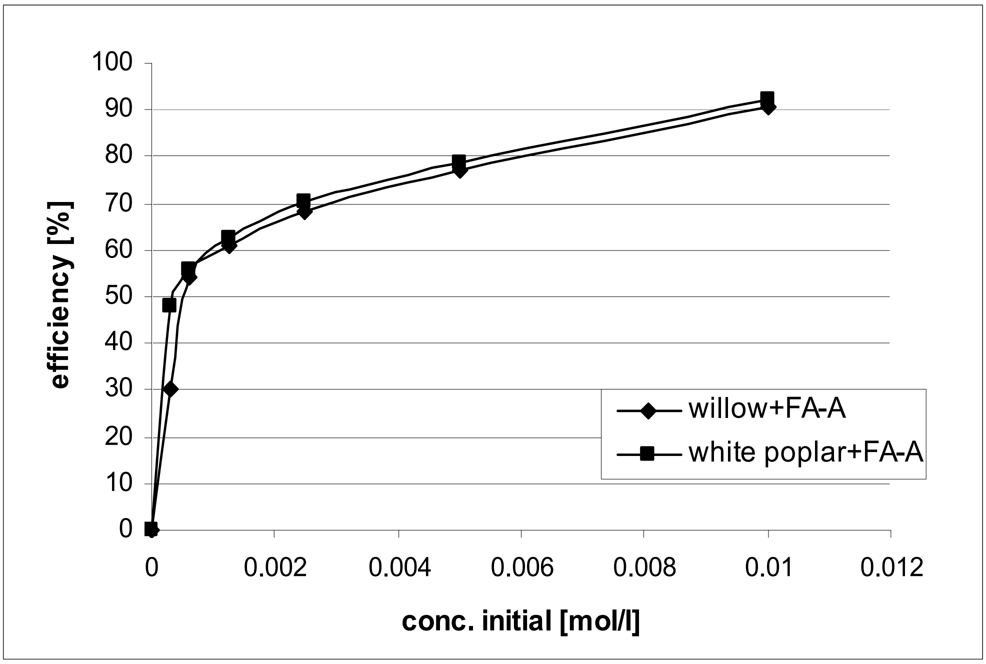


Fig. 5 – Influence of Cu(II) concentration on the adsorption efficiency on Sawdust: FA-A = 1:1.

The adsorption efficiency is lower at average concentrations but the substrate is highly efficient at copper concentrations close to 0.01mol/L. These data prove that the optimum substrate must be selected according to the heavy metal concentration. To elucidate the adsorption mechanisms, the adsorption isotherms were developed and are presented in Figs. 6 and 7.

The Langmuir model and the Freundlich equation were used to evaluate the mechanisms and estimate the adsorption parameters. The results are presented in Table 5.

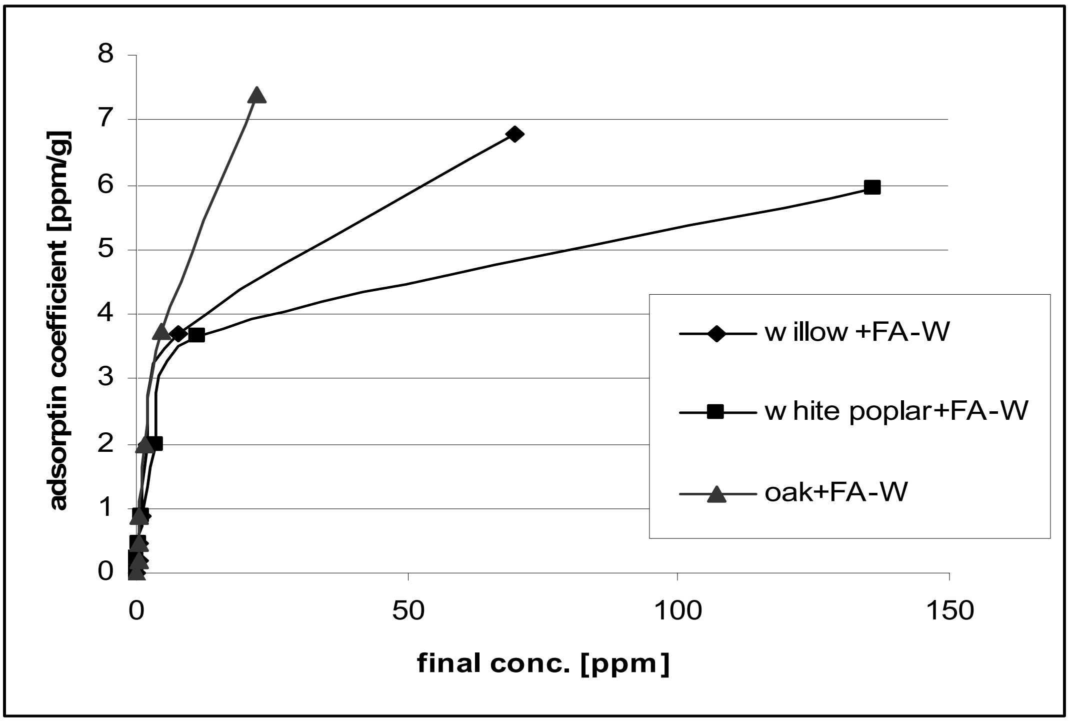


Fig. 6 – Adsorption isotherm of copper on sawdust: FA-W.

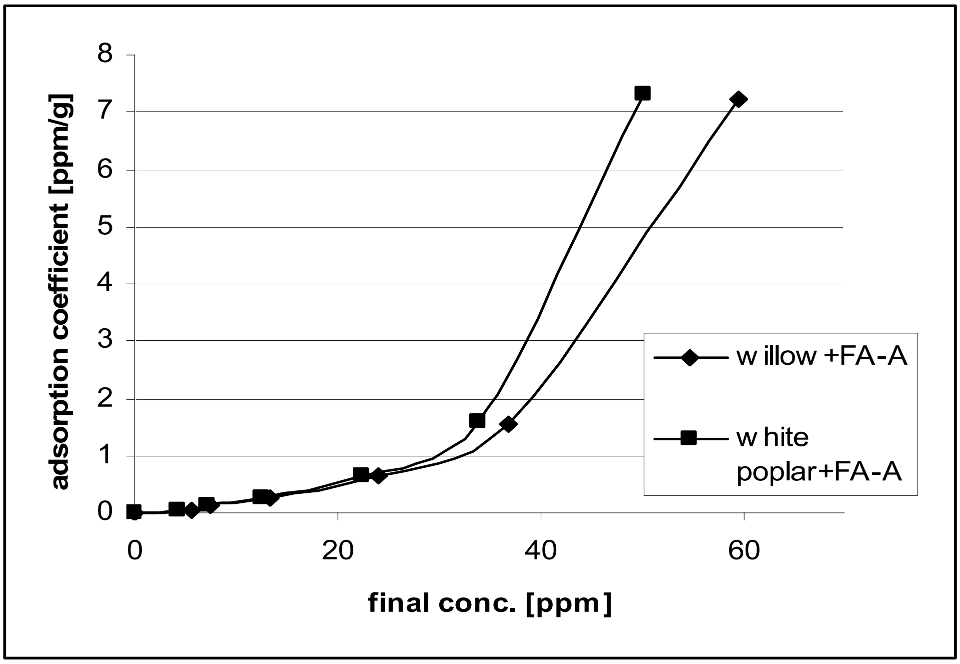


Fig. 7 – Adsorption isotherm of copper on sawdust: FA-A .

Table 5

Results modeling adsorption processes

Substrates	Langmuir			Freundlich		
	Γmax [ppm/g]	a	R^2	k	1/n	R^2
Willow + FA-W	7.7160	0.1066	0.9923	1.2527E-08	0.6414	0.8829
White poplar + FA-W	6.2305	0.1552	0.9993	9.463E-10	0.5029	0.9267
Oak + FA-W	11.1607	0.0924	0.8777	1.0007E-12	0.8026	0.9299
Willow + FA-A	-0.6512	-0.0200	0.8789	13520.26	1.8953	0.9675
White poplar + FA-A	-0.4628	-0.0188	0.5027	52369.09	2.0853	0.9767

As the data show, on the sawdust: FA-W substrate strong binding results between the substrate and the cation as described by the Langmuir equation, for willow and white poplar and the data confirm the efficiency results, proving the significant contribution of FA, with homogeneous adsorption sites.

On the substrates containing FA-A, adsorption is weak (the isotherm has a BET III shape) and could be well modeled using the Freundlich equation. Corroborating the isotherm and the efficiency data we may conclude that the amount of active adsorption sites is lower, and the sites have different adsorption affinities.

CONCLUSIONS

From these results, it can be concluded that the new substrates sawdust–fly ash for all sawdust types have promising efficiencies, on a broad concentration range of the investigated cation – copper. These indicate particular suitability of these substrates for the wastewater treatment. Responsible from these can be the changes of crystalline phases during the sawdust treatment.

The sorption isotherms of cooper ions from sawdust: fly ash washed with distilled water is well described by the Langmuir model. The maximum a sorption capacities, in decreasing order, corresponds to: oak +FA-W, (11.16 ppm/g); willow +FA-W, (7.72 ppm/g) and white poplar +FA-W, (6.23 ppm/g).

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