CHEMICAL ENGINEERING TRANSACTIONS
VOL. 53, 2016

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Valerio Cozzani, Eddy De Rademaeker, Davide Manca

ISBN 978-88-95608-44-0; ISSN 2283-9216
DOI: 10.3303/CET1653010

Study of Inorganic Pollution Sorption from Acidic Solutions by Natural Sorbents

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Anthropogenic activity has negative impact on the environment. Industrial waters are specific, because contains of contaminants that may destroy waste water treatment process. Finding of the new and cheap ways of treatment of wastewater contaminated by heavy metals can increase the quality of the environment in the affected localities and thus prevent adverse effects on fauna, flora or human beings. Sorption techniques belong to a cost effective methods that are able to effectively remove heavy metals. For the overall understanding of the sorption process, it is necessary to characterize and determine the properties of the used adsorbents.
The paper deals with the sulphate and metals (copper, zinc and iron) removal from acidic solutions by the various kinds of wood sawdust (poplar, hornbeam, spruce, pine, cherry, ash, and oak). The presence of hemicelluloses, cellulose and lignin in structure of wood sawdust was studied by infrared spectrometry. Poplar sawdust had efficiency of metal cations removal from aquatic model solutions approximately of 80.0 %. Hornbeam and poplar wood sawdust had 45.0 % efficiency of Cu, Zn and Fe removal at five times higher concentration of these metal cations. Hornbeam and cherry sawdust removed approximately 99.0 % of sulphate anions from solution with lower concentration of SO_4^{2-} (15 $mg.L^{-1}$) but at the concentration of sulphate approximately 80 $mg.L^{-1}$ sorption was ineffective.

1. Introduction

Contamination by inorganic compounds exists in aqueous waste streams from many industries, such as chemical and metal plating facilities, mining operations, and tanneries. The soils surrounding many military bases are also contaminated by metals and pose a risk of contamination for groundwater and surface water (Rengaraj et al., 2004). Among the metals associated with these activities also belong copper (Cu), zinc (Zn) and iron (Fe). Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Arora et al., 2004; Bailey et al., 1999). Treatment processes for water streams contaminated with metals include chemical precipitation, membrane filtration, ion exchange, carbon absorption, adsorption, and coprecipitation with adsorption (Petrilakova et al., 2014; Ramaraju et al., 2014; Sobhanardakani et al., 2013).
Cost effective alternative technologies or sorbents for treatment of metals contaminated waste streams are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration (Erto et al., 2013). Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability (Bailey et al., 1999). In general, a sorbent can be assumed as “low cost” if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Of course improved sorption capacity may compensate the low cost of additional processing. One of several available inexpensive natural sorbents (zeolites, clay, coal dust, peat, bark, etc.) is also wood sawdust. (Ali et al. 2012; Kadirvelu et al., 2001; Neto et al., 2013).

Please cite this article as: Balintova M., Demcak S., Singovszka E., Pagacova B., 2016, Study of inorganic polution sorption from acidic solutions by natural sorbents, Chemical Engineering Transactions, 53, 55-60 DOI: 10.3303/CET1653010

Adsorption heavy metals by wood sawdust are one of alternative methods to solve this kind of problems. Ahmad et al. (2009) studied sorption properties of natural organic sorbents and discovered that wood sawdust are formed complexes with a metal cations using their ligand or functional groups. The sorption of metals by sawdust might be attributed to their lignin, cellulose, carbohydrates, and phenolic compounds that have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions. Most cases have confirmed that the use of large quantities of wastes from agricultural products for the treatment of polluted water is an attractive and promising benefit for the environment (Larous S and Meniai, 2012).
The use of low-cost adsorbents like a wood sawdust as has been investigated as a replacement for costly current methods. Natural materials or waste products from certain industries with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost (Crini, 2006). Heavy metals are often discharged by a number of industries. This can lead into the contamination of freshwater and marine environment (Low and Lee, 2000; Bailey et al., 1999). Heavy metals are not biodegradable and have accumulation potential, causing various diseases and disorders (Bailey et al., 1999). It is well known that some metals are harmful to life, such as antimony, chromium, copper, lead, manganese, mercury, cadmium, etc. They are significantly toxic to human beings and ecological environments (Doris et al., 2000).
The aim of this article is a study of sorption properties of wood sawdust (hornbeam, poplar, pine, spruce, ash, cherry, and oak) for removal inorganic pollutions from model solutions (concentration of dissolved copper, zinc, and iron cations 10 and 50 mg.L^{-1}, respectively). Wood sawdust were analysed by infrared spectrometry for characterization of functional groups. Efficiency of sulphate and metal removal was analysed by colorimetric method.

2. Material and methods

Model solutions containing copper, zinc and iron cations, and sulphate anions were prepared by dissolution of their sulphate salts in deionised water. A Colorimeter DR890 (HACH LANGE, Germany) with appropriate reagents was used to determine concentration of dissolved copper, zinc, iron and sulphate.
For sorption poplar, hornbeam, ash, oak, cherry, pine, and spruce wood sawdust were used. For the purpose of wood sawdust efficiencies investigation, batch adsorption experiments were carried out. 1 g of each type of wood sawdust was mixed with 100 mL of model solutions containing 10 mg.L^{-1} and 50 mg.L^{-1} of copper, zinc and iron cations, respectively. After 24 hours reaction time, wood sawdust was removed by filtration through a laboratory filter paper for qualitative analysis, residual concentrations of appropriate ions were determined by colorimetric method and pH change was also measured by pH meter inoLab ph 730 (WTW, Germany). Also the % removal was calculated using the following equation:

$$\eta = \frac{(c_0 - c_e)}{c_0} \times 100\% \quad , \qquad (3)$$

where η is efficiency of ion removal (%), c_0 is the initial concentration of appropriate ions (mg.L^{-1}) and c_e, equilibrium concentration of ions (mg.L^{-1}).
Differences in FTIR measurements of all wood sawdust were carried out on Bruker Alpha Platinum-ATR spectrometer (BRUKER OPTICS, Ettingen, Germany). A total of 24 scans were performed on each sample in the range of 4,000–400 cm$^{−1}$.

3. Results and discussion

3.1 Infrared spectra of wood sawdust

The IR spectra of wooden sawdust show similar structure (Figure 1). The structure of wooden sawdust is mainly formed by hemicellulose, cellulose, and lignin (Kidalova et al., 2015). In Figure 1 can be seen the strong broad OH stretching (3300–4000 cm^{-1}), C–H stretching of methyl and methylene groups (2800–3000 cm^{-1}). The strong broad OH stretching at this area can be caused by the presence of water or moisture too. For hemicelluloses are typical the stretching band at 1731 cm^{-1} (presence of C=O from the acetyl groups) (Stevulova et al., 2014). For pine sawdust was observed the characteristic band at 1690 cm^{-1} which represents the occurrence of α, β–unsaturated aldehydes, ketones. Infrared spectra of lignin were observed by Zhang et al. (2015). The characteristic bands of lignin were confirmed at 1503 cm^{-1}, 1452 cm$^{−1}$ (aromatic skeletal vibrations of lignin) and at 1320 cm$^{−1}$ (syringyl and guaiacyl condensed lignin). Wavenumbers at 1422, 1367, 1315, 1153, 1024 and 894 cm^{-1} appertain to cellulose that occurs in two forms and this in crystalline (at 1315 cm^{-1}) and in amorphous (at 894 cm^{-1}). Functional groups of aromatics, carboxylic acids, alkyl halides were found at 828 cm^{-1} (Schwanninger et al., 2004). At 554 cm^{-1} were determined alkyl halides (C–Cl and C–Br strech) too. Band assignments according to the literature and band shifts are listed in Table 1 (Schwanninger et al., 2004; Stevulova et al., 2014).

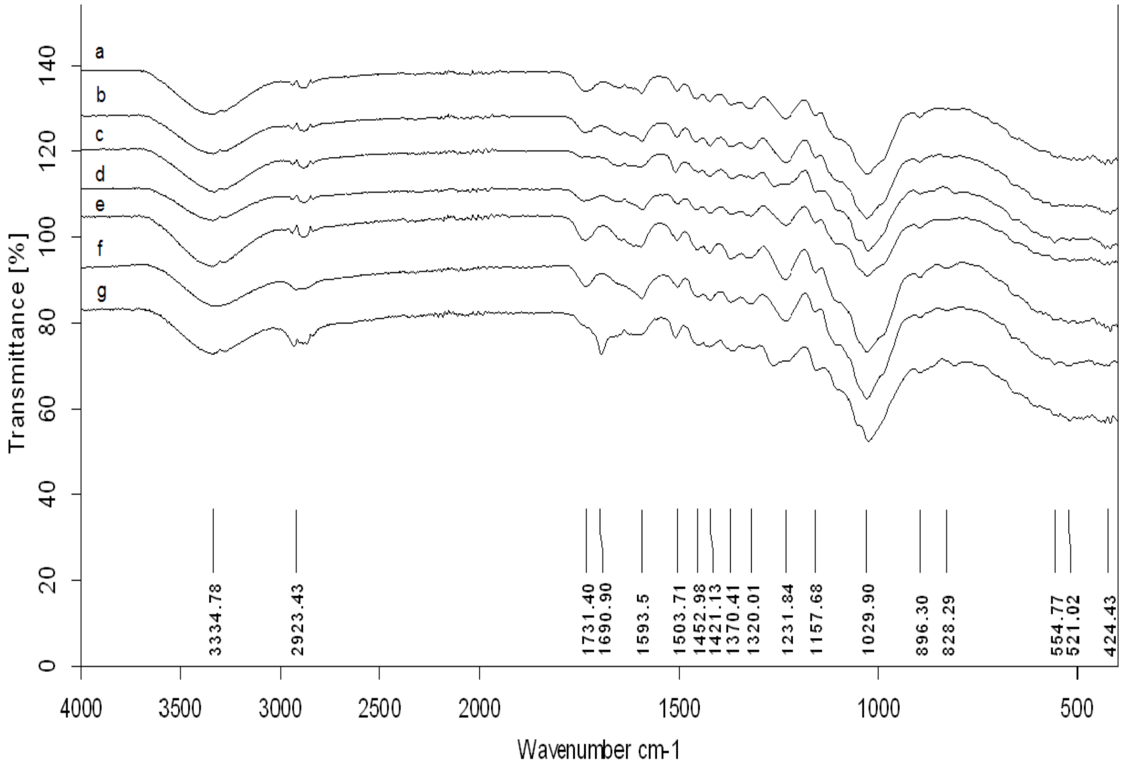

Figure 1: Infrared spectra of wooden sawdust: a-oak, b-ash, c-spruce, d-poplar, e-cherry, f-hornbeam and g-pine.

Table 1: IR bands assignment of functional groups in wood sawdust

Band position [cm^{-1}]	Functional group
3334	O–H stretch, H–bonded, N–H stretch
2923	C–H stretch, O–H stretch
1731	C=O stretch
1690	–C=C– stretch, N–H bend
1593	N–H bend, C–C stretch (in–ring)
1503	N–O asymmetric stretch
1452	N–O asymmetric stretch, C–C stretch (in–ring), C–H bend
1421	C–C stretch (in–ring)
1370	C–H rock
1320	C–N stretch, C–O stretch
1231	C–H wag (–CH2X)
1157	C–H wag (–CH2X), C–N stretch
1029	C–N stretch
869	=C–H bend,N–H wag, C–H “oop”
828	C–H “oop”, N–H wag, C–Cl stretch
554	C–Cl stretch, C–Br stretch

3.2 Sorption experiments

Results of sorption experiments for solution with concentrations of 10 $mg.L^{-1}$ cation are shown in Table 2. All kinds of wood sawdust used for sorption were capable to removal the ions. Bulut and Tez (2004) investigated of metals removal by various wood sawdusts as promising adsorbents for metals removal from wastewater with potentially more economical than current removal processes. Poplar and spruce exhibit the best effect on sorption of copper from solution with efficiencies above of 80 %. Hornbeam, ash, pine, cherry and oak have efficiencies in the range of 50.0 - 75.0 %. For zinc removal the best wood sawdust was poplar (75.0 %), hornbeam and spruce (70.0 %). The other kinds of wood sawdust exhibit efficiencies from 30.0 % to 50.0 %. Poplar and spruce wood sawdust was also the best sorbent for iron removal with efficiencies above of 70.0 %. But ash has the lowest efficiency for iron removal (47.0 %).

Concentration of sulphate in solution after sorption of metals was also determined. Hornbeam decreased the concentration of sulphate at the value less than 0.5 $mg.L^{-1}$ in solution of $CuSO_4$ and $ZnSO_4$, representing the efficiency of 99.0 %. In solutions of $FeSO_4$ the sulphate by ash and cherry was removed with high efficiencies. Changes of pH values in solutions were observed after sorption too. Due to different properties of Cu(II), Zn(II), and Fe(II) cations and different sawdust materials, the adsorption took place in a slightly different pH range for different metals. Shukla et al. (2002) observed that In a certain pH range for a one specific metal cation may be one or more a of species present in a form (M, MOH^+, $M(OH)_2$, etc.) at a solution. At lower pH, the positive charged metal ion species may compete with H^+ and be absorbed at the surface of the sawdust by ion exchange mechanism. At elevated pH, mainly neutral, metal cations may be absorbed by hydrogen bonding mechanism along with ion exchange. Sorption of Cu(II), Zn(II) and Fe(II) by a hornbeam and poplar increase of value pH. Possibility of ion exchange between dissolved metal cations in and H^+ from sawdust (spruce, ash, pine, cherry, and oak) was indicated by decreasing of pH.

Table 2: Results of sorption experiments with wooden sawdust (initial concentration of cations in solutions c_0=10 $mg.L^{-1}$)

Sorbents materials	Initial concentration $c_0(Cu^{2+})$=10 $mg.L^{-1}$ and $c_0(SO_4^{2-})$=15.1 at pH=5.8			Initial concentration $c_0(Zn^{2+})$=10 $mg.L^{-1}$ and $c_0(SO_4^{2-})$=14.7 at pH=5.4			Initial concentration $c_0(Fe^{2+})$=10 $mg.L^{-1}$ and $c_0(SO_4^{2-})$=17.2 at pH=5.4		
	$c_e(Cu^{2+})$ [$mg.L^{-1}$]	$c_e(SO_4^{2-})$ [$mg.L^{-1}$]	pH	$c_e(Zn^{2+})$ [$mg.L^{-1}$]	$c_e(SO_4^{2-})$ [$mg.L^{-1}$]	pH	$c_e(Fe^{2+})$ [$mg.L^{-1}$]	$c_e(SO_4^{2-})$ [$mg.L^{-1}$]	pH
Hornbeam	2.72	<0.5	5.2	3.2	<0.5	5.9	3.7	17.2	5.5
Poplar	1.42	5.3	5.3	2.6	14.7	5.8	2.2	11.9	5.7
Spruce	1.9	12.3	4.9	3.0	14.7	5.3	3.0	17.2	5.0
Ash	5.0	15.1	5.4	4.7	14.7	5.0	5.3	1.9	5.8
Pine	4.0	10.5	4.6	7.0	14.6	5.1	4.4	14.7	4.8
Cherry	2.3	11.0	4.9	6.0	14.7	5.2	4.0	<0.5	5.0
Oak	4.9	14.1	4.1	5.7	14.7	4.4	5.1	14.2	3.7

This study was compared with determination of the efficiency of removal cations with five times higher concentrations. Table 3 presents the efficiency of metal cations removal from these solutions. Hornbeam and poplar have the best efficiency (approximately 45.0 %) for copper, zinc and iron removal. Ash has the 40.0 % efficiency for zinc and iron removal. The lower values of cations removal from solutions can by caused by a lower sorption capacity of wood sawdust. Surprisingly, the concentration of sulphates in these solutions remained practically unchanged.

Also in this case changes of pH values in solutions were observed after sorption. Values of pH after sorption by sawdust were decreased in all causes. We can suppose that oak sawdust iron(II) from solution shows intensive ion exchange which is declared by a intensive decreasing at a pH=3.0. More significant changes of pH was observed in sorption of Cu(II) and Zn(II) from solutions by oak sawdust too.

Table 3: Results of sorption experiments with wooden sawdust (initial concentration of cations in solutions c=50 $mg.L^{-1}$)

Sorbents materials	Initial concentration $c_0(Cu^{2+})$=50 $mg.L^{-1}$ and $c_0(SO_4^{2-})$=75.5 at pH=4.7			Initial concentration $c_0(Zn^{2+})$=50 $mg.L^{-1}$ and $c_0(SO_4^{2-})$=73.5 at pH=5.1			Initial concentration $c_0(Fe^{2+})$=50 $mg.L^{-1}$ and $c_0(SO_4^{2-})$=86.0 at pH=4.8		
	$c_e(Cu^{2+})$ [$mg.L^{-1}$]	$c_e(SO_4^{2-})$ [$mg.L^{-1}$]	pH	$c_e(Zn^{2+})$ [$mg.L^{-1}$]	$c_e(SO_4^{2-})$ [$mg.L^{-1}$]	pH	$c_e(Fe^{2+})$ [$mg.L^{-1}$]	$c_e(SO_4^{2-})$ [$mg.L^{-1}$]	pH
Hornbeam	28.7	75.2	4.5	25.6	73.1	5.0	26.8	85.5	4.5
Poplar	28.5	75.4	4.6	26.3	73.4	5.0	26.6	85.7	4.8
Spruce	39.2	75.4	4.4	31.3	73.4	4.8	34.0	85.8	4.7
Ash	39.2	75.5	4.7	29.8	73.5	4.9	30.4	69.8	4.2
Pine	41.4	75.3	4.1	36.2	73.4	4.7	37.8	85.9	4.4
Cherry	37.6	75.4	4.3	33.3	70.1	4.9	31.4	80.2	4.0
Oak	36.2	75.2	3.5	35.8	73.2	4.1	31.8	85.4	3.0

4. Conclusions

The use of low cost natural sorbents as a replacement of current costly methods heavy metals removal from solution is increasing in recent years. Natural materials or waste products from industry with a high capacity for heavy metals removal can be obtained, employed, and disposed of with a little cost. Sawdust, as a low-cost organic sorbent material, has been proven as a promising material for the removal of metals (Cu, Zn and Fe) from waste waters.

The function groups of wood sawdust were characterized by infrared spectra that confirmed the presence of hemicelluloses, cellulose and lignin (aromatic skeletal vibrations of lignin syringyl and guaiacyl condensed lignin). All kinds of wood sawdust exhibited the same behaviour. In case of pine wood sawdust was observed the α,β–unsaturated aldehydes, ketones with wavenumber at 1690 cm^{-1}.

Wood sawdust has been shown as suitable product for removal metals from solutions. The best properties had poplar in solution with cations concentration of 10 $mg.L^{-1}$ copper, zinc and iron and their removal exhibited efficiency about of 80.0 %. In case of five times higher metal cations concentration the best sorption properties had hornbeam and poplar. At lower concentrations of sulphate in zinc and copper solution hornbeam removed approximately 99.0 % of sulphates, the same efficiency had cherry at removal sulphate from iron solution.

Changes of values pH showed the processes of adsorption and ion exchange. In case removal iron(II) by a oak sawdust (initial concentration 50 $mg.L^{-1}$) was decreased pH from 4.8 to 3.1, which was probably caused by an intensive ion exchange. Increased pH values were observed on zinc and iron removal by a hornbeam and poplar.

The sorption experiments showed a potential of the wood sawdust, especially poplar's sawdust, to remove cations from model acidic solutions. Adsorption efficiencies were influenced by the initial cations concentration, pH of model solutions and kind of sorbent used on adsorption experiments. The results from experiments also provide promising perspectives for the utilization of wood sawdust as a biosorbent for reducing metal pollution in wastewaters and they showed potential to be used on an industrial scale.

Acknowledgments

This work has been supported by the Slovak Grant Agency for Science (Grant No. 1/0563/15).

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