Recovery of an Agro-industrial Vinasse by Adsorption on Different Wood Materials: Parametric Study at Laboratory Scale

Guillaume Daragon, Gwenaëlle Trouvé,* Cornelius Schönnenbeck, and Gontrand Leyssens

Three types of biomasses (miscanthus, spruce, and a mixture of different woodchips species) were tested as low-cost adsorption media for an industrial agro-industrial effluent, typically a vinasse. Influences of effluent dilution, working temperature, and time duration were studied. Kinetic modelling studies of adsorption were proposed. Ratios of adsorption at ambient temperature and without dilution expressed in g of dry vinasse per g of dry biomass were 1.0, 0.85, and 0.65 for miscanthus, woodchips mixture, and spruce, respectively. An increase of the temperature from 10 °C to 50 °C led to a decrease of the vinasse viscosity and favored its penetration in the biomasses. Maximal adsorbance of dry matter of vinasse was obtained at 50 °C for a vinasse viscosity of 20 mPas. Whatever the experimental conditions required during adsorption processes, miscanthus showed the best affinity for the vinasse. Pseudo-second order and intra-particle diffusion model well described the adsorption process. This study indicates that conventional biomasses could be used as natural low-cost adsorbent for by-products such as vinasse.

Contact information: *Laboratoire Gestion des Risques et Environnement, Institut de Recherche J.B. Donnet, 3 bis, rue A. Werner 68093 Mulhouse, France, *Corresponding author: gwenaelle.trouve@uha.fr*

INTRODUCTION

Since several years back, clever management of energy and resources has been implemented on a massive scale. One of the most important points concerns water utilization, and this will remain the most serious challenge for future generations. Therefore, research for clean, safe, and economically feasible technologies for wastewater treatment have reached a prominent place in order to reduce impacts of human activity on the environment. Wastewater treatment plants have been improved and designed to treat a range of effluents from different origins (domestic or industrial). However, some of them are more complex fluids, such as organic effluents from food, agro, or textile industries for instance. These effluents typically have high chemical oxygen demand (COD) values, high organic load (amino-acids, polyphenols, tannins, fatty acids, *etc*.), and may also contain toxic components and severe pollutants such as heavy metals. These chemical and physical properties disallow direct discharge into natural media since they may cause strong (even irreversible) damage to the environment, such as the eutrophication of rivers if ejected into aquatic media or soil denaturing if spread on the fields.

Adsorption on activated carbon is a current technology that can be used to remove pollutants from wastewater. This technique is very interesting because of the high efficiency of the material and its huge specific surface area (Hubbe *et al.* 2014). Heavy metal removal is widely documented in the literature (Mohan and Pittman 2006; Rao *et al*.

2006; Hubbe *et al.* 2011). However, the use of activated carbon still remains relatively expensive, and steps of support regeneration are needed after several cycles of adsorption to recover the initial capacity. Thus, many authors have focused their attention on new types of adsorbents based on biomass and other kinds of low-cost supports such as sludge, clay, fly ash, and chitosan materials (Babel and Kurniawan 2003; Shin *et al.* 2007; Naiya *et al*. 2009; Quasim and Mane 2013; Aziz *et al*. 2014). In recent years, many authors have focused their attention on using biomass for effluent treatment. Indeed those materials such as wood, sawdust, bark, straw, or even sludge are widely available and cost-effective. Due to their good adsorption properties, they are considered an interesting adsorption support alternative (Yu *et al*. 2003; Grini 2005; Aziz *et al*. 2014). For example, biomasses like sawdust, woodchips, bark, straw, and leaves also present good adsorption properties for many pollutants such as fluoride (Yadav *et al*. 2013) or heavy metals such as chromium (Yu *et al*. 2003), lead (Reddy *et al*. 2010; Gundogdu *et al*. 2009), and even arsenic and mercury (Sud *et al*. 2008). Others have studied adsorption for far more complex compounds like dyes from textile and leather industries on peanut husks or on sawdust (Kausik *et al*. 2009; Noreen *et al*. 2013), dyes such as methylene-blue from the paper industry on different agricultural wastes, clays, and zeolites, or even pesticides on sugarcane, bagasse fly ash, and rice husk (Akhtar *et al*. 2007; Rafatullah *et al*. 2010). Since biomass is cheap, widely available, renewable, and often a byproduct itself (from agriculture or wood industry), it is considered a promising alternative (Nguyen *et al*. 2013).

Agro-food industrial processes lead to large amounts of by-product as vinasse (Carrocci *et al.* 2012; Christofoletti *et al*. 2013). Vinasse is generally used as an additive for animal feed because it contains a large fraction of organics (proteins, pectins, polyphenols, and colored compounds) and as a fertilizer because its mineral composition is rich in NPK elements. Recently its demand may be limited in such potential applications by strict environmental restrictions. Vinasse is an acid by-product with high COD (30-60 g L^{-1}) containing a large fraction of organics as proteins, pectins, polyphenols, and melanoïdins (Caqueret *et al*. 2008). Therefore, there has recently been an increase of interest in recovering valuable components from distillery vinasse.

By-product effluents as vinasses are mostly adsorbed onto activated carbons (Caqueret *et al*. 2008) or by initial clarification by gravity followed by secondary treatment with activated sludge (Vaccari *et al*. 2005; Yang and Li 2013). The main objective of this work was to study the natural adsorbent capacities of three different biomasses by adsorption as low cost adsorbents with a vinasse (organic by-product from sugar industry with high COD), without any biomass chemical pre-treatment, in order to recover the dry matter parts for energy recovery. The amount of dry matter taken from vinasse was followed by simple ratio calculations. Different adsorption conditions were tested in order to reach the highest adsorption yields of organic matter possible. The study of adsorption equilibrium and kinetics is essential to supply the basic information required for the design of an adsorption process.

EXPERIMENTS

Materials

Two wood samples (spruce and wood chips) and one energetic crop (miscanthus) were chosen for this study. Spruce (Spc) was manufactured by AGRIVALOR SA (Bergheim, France) and represented wood from the Alsatian forest. Forest chips of miscanthus (Msc) were harvested and sieved around the south of Alsace in the village of Ammertzwiller. Wood chips are produced from European forests and are a mixture (Mix)

of different woods with spruce representing 70% of the total mass. The 30% left is composed of fir, pine, oak, and beech, of which the different proportions depend on the countries of Europe where the trees were harvested. As shown in Fig. 1, Mix and Spc based materials are woodchip byproducts from the sawmill industry. Raw Msc is a grass sold as straw.

Fig. 1. Biomass external aspects (A: Msc, B: Spc, C: Mix)

Physical and chemical characterizations of the different samples were performed through the ultimate analyses as well as apparent porosity and bulk densities, relative moisture, and ash contents. The ultimate analyses of samples were carried out by the SOCOR laboratory (Dechy, France) to determine carbon, hydrogen, oxygen, nitrogen, chlorine, and sulfur weight fractions. Ash content had been established using a muffle furnace at two different temperatures according the NF-EN-14775 norm. Two protocols were compared; in the first one samples were heated at 550 °C for 2 h (with a burning stage at 250 °C for 1 h), and in the second protocol they were heated at 815 °C for 3 h. Water contents were determined after drying biomass samples at 105 °C according to the NF-EN-14774 norm. Bulk densities were determined using a beaker whose mass and volume were precisely known and filled with uncompressed biomass.

In this study, the industrial agro-effluent was a vinasse obtained from the final phase of alcohol fermentation, characteristic of the agro-food industry. It was used as received, and it contained 57% by weight of dry matter. A known volume weighing had been done in order to determine its density. The dynamic viscosity μ was measured using a falling-sphere viscometer.

Adsorption Protocol

Adsorption experiments on raw materials (as received) as shown in Fig. 1 were performed, and adsorption ratios were obtained with relatively high standard deviations, mainly due to both variation of humidity during different storage conditions and various particle sizes. Size distribution was determined first. In order to study the influence of particle size on adsorption ratios, based materials were calibrated using different sieves with particle diameters (d) ranging from less than 1 mm to over 20 mm. The influence of parameters on adsorption ratios as dilution ratio, temperature, and step duration were only evaluated for size fractions of 4 to 9 mm in order to increase the accuracy of the protocol.

Based materials were ground and sieved to meet the size range of 4 to 9 mm and then dried in an oven at 105 °C. Kinetic modelling was also studied for this size fraction. 10 g of each dry sample (8 g for Msc) were each put in 80 mL of vinasse in 100 mL beakers for 2 h; they then were drained for 2 h to finally be dried at 105 °C in an oven for 24 h. Results given in the parametric study are the mean of at least three experiments. The bars in the following figures represent the standard deviations.

Calculations of Adsorption Ratios

Two different adsorption ratios $R_{dm}{}^{[vns/bio(i)]}$ and $R_{dm}[^{vns/bio(f)}]$ were calculated according the following equations (Eqs. 1 and 2),

$$R_{dm}^{[vns/bio(i)]} = \frac{\left(m_{bio}^{[Ads,Drn, Dry]} - m_{bio}^{[Dry]} \right)}{m_{bio}^{[Dry]}} \tag{1}$$

$$R_{dm}^{[vns/bio(f)]} = \frac{\left(m_{bio}^{[Ads,Drn, Dry]} - m_{bio}^{[Dry]} \right)}{m_{bio}^{[Ads,Drn,Dry]}} \tag{2}$$

Where $m_{bio}{}^{[Dry]}$ is the mass of dry biomass (m_{bio}) before adsorption (g), $m_{bio}{}^{[Ads,Drn]}$ is the mass of the biomass after adsorption and draining, $m_{bio}{}^{[Ads,Drn,Dry]}$ is the mass of the biomass after adsorption, draining, and drying processes. The difference given in the following Eq. 3 represents the mass of dry matter of vinasse $m_{dm}{}^{[Ads]}$ adsorbed on dry biomass:

$$m_{dm}^{[Ads]} = (m_{bio}^{[Ads,Drn,Dry]} - m_{bio}^{[Dry]}) \tag{3}$$

$R_{dm}{}^{[vns/bio(i)]}$ (g vinasse dry/ g initial biomass dry) indicates the dry matter part of the vinasse adsorbed on the dry biomass support. $R_{dm}{}^{[vns/bio(f)]}$ (g vinasse dry/ g final dry biomass after adsorption) represents the part of dried matter of vinasse adsorbed on the dry mixture (dry vinasse + dry biomass) after adsorption. Measurement of the bulk density was done using a beaker whose mass and volume were known and then filled with uncompressed biomass. The dynamic viscosity μ was measured using a falling-sphere viscometer.

RESULTS AND DISCUSSION

Physical and Chemical Properties of Biomass Types

Table 1 shows both the chemical characteristics and the particle size distributions of biomasses. Particles in the size ranges of over 20 mm and 20 to 2.5 mm constituted the main part of the total mass for Mix, Msc, and Spc with proportions ranging from 95% to 98%.

Table 1. Physical and Chemical Characteristics of Biomasses

	Msc	Mix	Spc	Vinasse
	Chemical characteristics[a]			
C (%)[a]	48.70	49.94	50.50	41.65
H (%)[a]	5.89	6.06	5.97	4.30
O (%)[a]	43.67	45.35	42.22	33.19
N (%)[a]	< 0.30	< 0.10	< 0.30	3.92
S (%)[a]	0.12	< 0.3	0.06	0.26
Cl (%)[a]	0.16	< 0.0005	0.09	0.44
P (ppm)[a]	345	nd	< 200	2900
Ca (ppm)[a]	6 700	nd	6 200	14 000
K (ppm)[a]	3 300	nd	1 600	87 100
Mg (ppm)[a]	450	nd	920	1 140
Na (ppm)[a]	82	nd	156	35 700
Atomic O/C ratio	0.67	0.68	0.63	0.60
Atomic H/C ratio	1.45	1.45	1.42	1.24
COD (mg L^{-1} O$_2$)[b]	--	--	--	520 000
Organic Carbon (g kg^{-1} DM)[c]	--	--	--	325
	Particle size distributions			
D >20 mm	0.2	10.0	11.9	--
20 mm >D >9 mm	39.4	47.8	66.9	--
9 mm >D> 6 mm	38.1	19.9	11.7	--
6 mm >D >4 mm	11.4	10.9	5.1	--
4 mm >D >3.15 mm	5.4	3.5	2.4	--
3.15 mm >D >2.5 mm	0.1	2.5	0.3	--
2.5 mm >D >2 mm	0.3	1.6	0.3	--
2 mm >D >1.6 mm	0.8	1.6	0.5	--
1.6 mm >D >1.25 mm	1.0	0.9	0.3	--
1.25 mm >D >1 mm	0.2	0.4	0.1	--
D <1 mm	3.1	1.6	0.5	--
a: on dry basis; b: standard NFT-90-101; c: standard NF ISO 14235; n.d.: not determined				

Compared with literature data concerning wood biomass, energy crops, and agricultural by-products (corn, rice straw, and shell), these materials were found to have typical compositions (Senneca *et al*. 2007; Jeguirim *et al*. 2010; Verma *et al*. 2012). Weight fractions of the different elements (C, H, O, N, and S) samples were in the same order of magnitude as those reported for conventional lignocellulosic materials (Johansson *et al*. 2005). The elemental analysis of the studied vinasse was close to those of distillery and olive mill oil extraction effluents in terms of COD and the amount of organic carbon (España-Gamboa *et al*. 2011; Chouchene *et al*. 2012). With O/C and H/C atomic ratio values at 0.60 and 1.24, respectively, this vinasse can be classified as biomass according to the Van Krevelen diagram (Senneca 2007; Koppejan and Van Loo 2008). These ratio values are very close to those of the three lignocellulosic materials (Msc, Mix, and Spc) used as adsorption support.

However, chlorine content in the vinasse appeared to be high and would enhance the amount of this element in the mixture after adsorption. Table 2 gives physical properties.

Table 2. Physical Characteristics of Biomass Types

	Msc	Mix	Spc	Vinasse
pH	--	--	--	7.2
density	--	--	--	1.25
ρ_b (kg.m^{-3})[a]	116	148	286	--
ε (%)[a]	44	n.d	52	--
μ (mPa.s) at 20°C	--	--	--	60.6
Moisture (%)[a]	10	39	44	43
Ash at 550°C (%)[a]	1.40	0.6	0.12	16.50
Ash at 815°C (%)[a]	1.24	0.4	0.15	10.20
a: on raw basis; n. d.: not determined				

Msc presented the lowest humidity content related to its fine structure of straw. Humidity contents for Mix and Spc were very close to those of biomass in district heat production facilities. The vinasse presented ash content very close to those of distillery effluents found in literature (Robertiello 1982; España-Gamboa *et al*. 2011, Christofoletti *et al.* 2013). Calcination at different temperatures did not significantly influence the ash content for Msc, Mix, and Spc. The vinasse presented high ash content whatever the temperature of calcination, and there was a significant difference between calcination at 550 °C and 815 °C. This was probably due to two phenomenons: organic compounds still remained at 550 °C, and/or an increase of temperature to 815 °C could have involved the devolatilization of some mineral fractions, such as sodium and potassium combined with chlorine and sulphur under their chloride and sulphate salts.

Wood densities are generally relatively variable even for the same wood species depending on wood origin, cutting period, and tree age. Indeed, densities could even be different within the same trunk, depending on which part of the wood is analyzed, whether sapwood (beneath the bark) or heartwood (also called duramen). Despite that, the results were close to those found in other publications. Densities of beech and spruce were close to those of wood chips (550 kg m^{-3}) and wood pellets (693 kg m^{-3}) (Senneca *et al.* 2007; Verma *et al.* 2012). Concerning dry silage miscanthus, its density was close to 0.12 g cm^{-3} in agreement with the literature (Lewandowski *et al.* 1995; Lisowski *et al*. 2011). Value of the density of liquid vinasse (1250 kg m^{-3}) is slightly higher than those found for other agro-food effluents with values varying in the range 1010 to 1060 kg m^{-3} (Robertiello 1982).

Parametric Study of the Adsorption Process
Influence of biomass particle size
The influence of biomass particle size was studied under standard conditions (adsorption time 2 h and draining time 2 h) at room temperature (20 °C). Adsorption of biomasses was done on different distribution sizes representing the main part of the biomass mass from 20 mm to 3.15 mm. Fractions below 3.15 mm represented less than 8% of the total mass. A high relative standard deviation was observed for the biggest particle size of miscanthus (>20 mm). This size fraction only consisted of 0.2% of the total mass (*i.e.*, Table 1), and the value of $R_{dm}[^{vns/bio(f)}]$ was not included in Fig. 2.
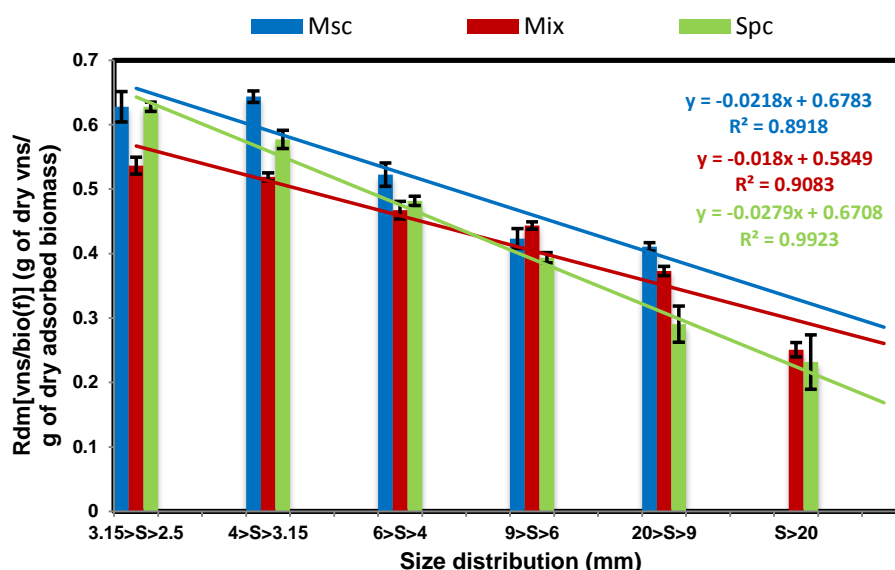
Fig. 2. Influence of the size distribution on $R_{dm}[^{vns/bio(f)}]$

Regarding standard deviations, one tendency appeared to indicate an influence of the size particles on adsorption ratios, particularly between 3.15 and 9 mm. These results confirm that the smaller the chip is, the better the dry matter adsorption is. Values of linear correlation ratios R^2 are 0.9923, 0.9083, and 0.8918 for Spc, Mix, and Msc, respectively.

Influence of effluent dilution

Dilution could theoretically lead to better circulation and penetration within the chips and water could act as an adsorption vector for big molecules of the vinasse. Effluent was diluted at 20 °C from 0 (raw) to 80 % (vol/vol) with demineralized water. The influence of the dilution of the vinasse was performed in the standard conditions with an adsorption time of 2 h and a draining time of 2 h at 20 °C. Results of $R_{dm}[^{vns/bio(i)}]$ and $R_{dm}[^{vns/bio(f)}]$ are presented in Fig. 3.
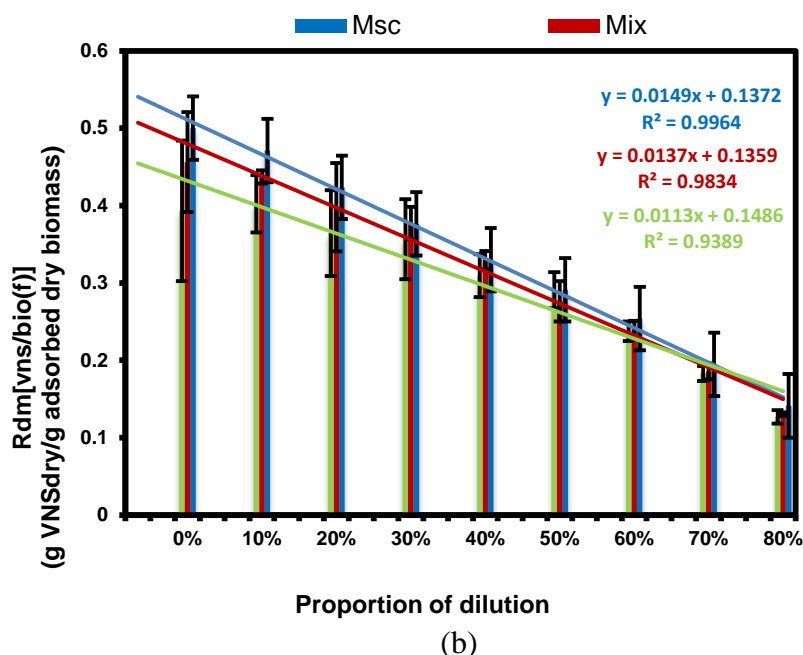

(a)

(b)
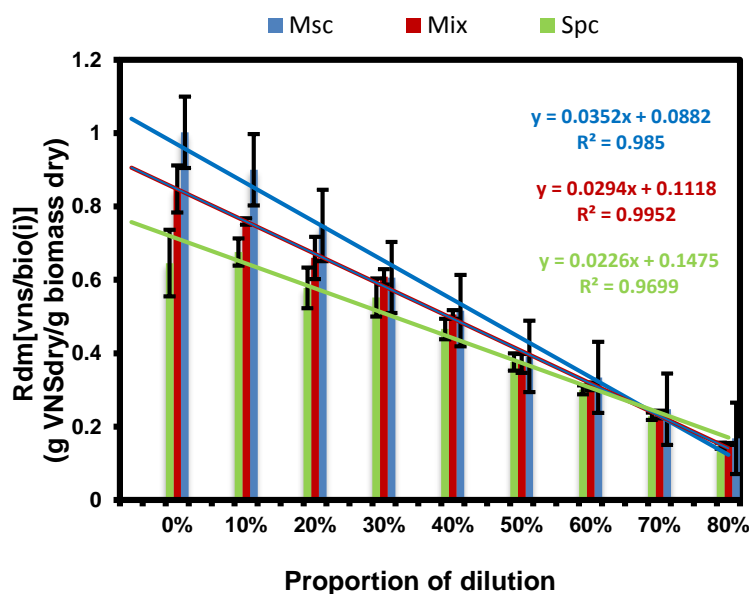
Fig. 3. Influence of the dilution on the adsorption ratios a: $R_{dm}[^{vns/bio(i)}]$ and b: $R_{dm}[^{vns/bio(f)}]$

As shown in Fig. 3, there was a linear decrease in dry matter supply as the dilution level increased. These results were expected because the dilution acted to decrease the amount of matter in the total volume. Linear correlation ratio R^2 values were in the range of 0.938 to 0.996 for both ratios. When dilution ratio is higher than 10%, differences between biomass varieties are not more significant regarding the standard deviations of repeated experiments for both $R_{dm}[^{vns/bio(i)}]$ and $R_{dm}[^{vns/bio(f)}]$. At low dilution levels (0 and 10%), ratios values ($R_{dm}[^{vns/bio(i)}]$) varied with the biomass variety. Without dilution, a maximum of 50% of dry matter of vinasse could be adsorbed on Msc. Spc seems to have less affinity for by-product as vinasse. Because the Mix sample is a mixture of wood varieties in which spruce dominates, its adsorption behaviour is found to be between these of Msc and Spc.

Effluent dilution had only poor effects on dry matter adsorptions, and vinasse adsorption seemed to be mostly a surface phenomenon. Surfaces and section photos were shot using a binocular microscope with 20x magnification to observe any changes in the structure of Msc and Spc before and after adsorption with concentrated vinasse. Figures 4 and 5 compare surfaces and cross-sections for Msc and Spc before and after adsorption by non-diluted vinasse, respectively. The raw cross-section of Msc is the only image given with the higher, 40x magnification.
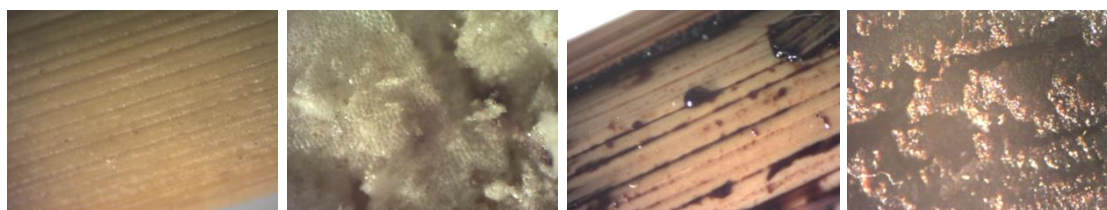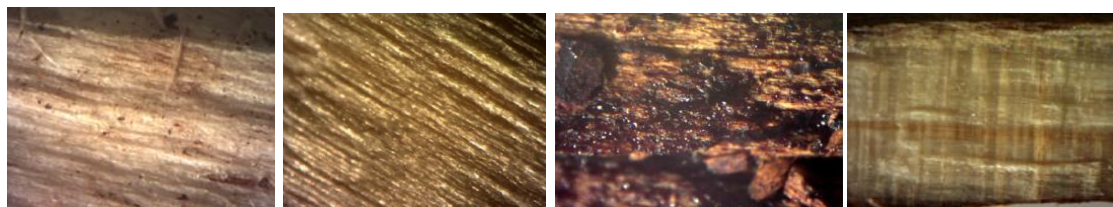

Fig. 4. Msc images (from left to right: raw surface and cross-section (×40); surface and cross-section after adsorption)

Optical inspection of biomass after adsorptions showed a heterogeneous structure. Vinasse residues seem to have been fixed at the outer surface or in pores of the biomass.

The cross-section of Msc was well defined by a honeycomb-shaped internal structure that allowed good penetration of the vinasse compared to the external surface where it was mainly in the grooves.


Fig. 5. Spc images (from left to right: raw surface and cross-section; surface and cross-section after adsorption)

The adsorption phenomenon was found to be quite different for spruce. Adsorption of vinasse was favoured on the wood surface. With a higher bulk density for Spc than Msc, penetration was limited *via* the cross-section for Spc. Msc reached the highest values of adsorption ratios due to its widely porous and honeycomb-shaped internal structure.

Influence of working temperature

The influence of temperature was evaluated with non-diluted vinasse under the standard conditions (adsorption time of 2 h and draining time of 2 h). An increasing working temperature should decrease the vinasse viscosity and may favor the increase of dry matter ratio in the biomass. Adsorptions of this effluent on biomasses were tested in the temperature range 10 °C to 80 °C. Figure 6 shows the evolution of $R_{dm}[^{vns/bio(i)}]$ and $R_{dm}[^{vns/bio(f)}]$ versus temperature during the adsorption process.
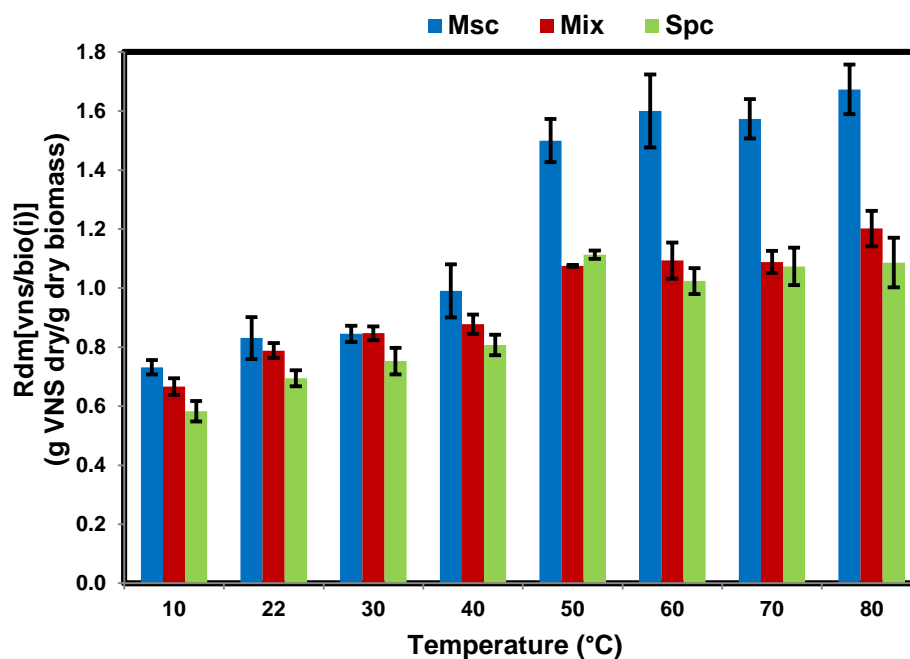
(a)
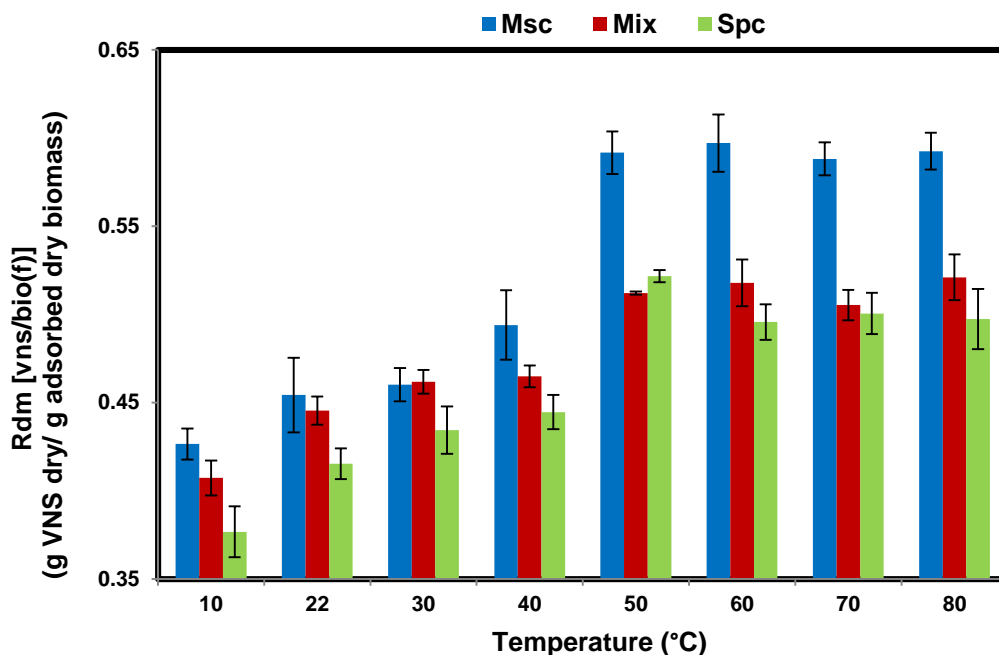
(b)

Fig. 6. Influence of the temperature on adsorption ratios (a: $R_{dm}[^{vns/bio(i)}]$ and b: $R_{dm}[^{vns/bio(f)}]$)

      Adsorption ratios of the dry matter part of the vinasse are shown in Fig. 6. From 10 °C to 50 °C, there was a slight increase for dry matter adsorption with the increase of temperature, mainly for Msc and Spc. The enhancement in adsorption for temperatures between 10 °C and 50 °C could be due to the decrease of the viscosity of the vinasse of 80 mPas at 10 °C to 20 mPas at 50 °C. This could increase the mass transfer in the boundary layer of the adsorbate. Moreover, this may also be a result of an increase in the mobility of the vinasse and then in an increase of intra-particle diffusion of sorbate with the rise of temperature. At higher temperatures, the total quantity adsorbed is not temperature dependent. This is in accordance with the mechanism of physical adsorbance – at higher temperatures adsorbance decreases (exothermic reaction). Meanwhile, changes of viscosity at temperatures over 50 °C were small (viscosity versus temperature follows a negative exponential law), and then the global adsorption efficiency was stable for this temperature range. Adsorption ratios are compared for both temperatures 10 °C and 50 °C in Table 3 and yields are calculated. Yield is defined by the ratio of Rdm (50 °C)/Rdm (10 °C).

Table 3. Comparison of Ratios $R_{dm}[^{vns/bio(i)}]$ and $R_{dm}[^{vns/bio(f)}]$ at 10 °C and 50 °C

	Msc	Mix	Spc
Rdm[vns/bio(i)] (mg g^{-1}) at 10 °C	730	670	580
Rdm[vns/bio(i)] (mg g^{-1}) at 50 °C	1500	1080	1110
Yield	2.0	1.6	1.9
Rdm[vns/bio(f)] (mg g^{-1}) at 10 °C	430	410	380
Rdm[vns/bio(f)] (mg g^{-1}) at 50 °C	590	510	520
Yield	1.4	1.2	1.4

An increase in temperature from 10 °C to 50 °C had a positive effect on ratios and was particularly significant for biomass as Msc and Spc. Yields for both ratios presented the same values for Msc and Spc. Samples containing several types of biomass species as Mix (30% of the total mass were not known) gave lower yield values. This fact pointed out the main influence of the 30% of unknown species in the Mix woodchips.

Adsorption Kinetic Modelling Studies

Experimental data were recorded at room temperature (20 °C) with the variation of the adsorption time from 0.5 h to 16 h. Draining time was standardized at 2 h, and after the adsorption process samples were dried in an oven at 105 °C for 24 h. Kinetic studies are essential here because they reveal the uptake rate of adsorbate, which controls the residual time for the entire adsorption process (Demirbas 2008).

Adsorption can be described by different models. The Lagergren's pseudo first order, the pseudo second order, and the intraparticle diffusion models were used to describe the adsorption mechanism of vinasse on the three biomass supports. Kinetic data in the following Figs. 7 to 9 represent the mean values of at least three experiments.

The first order adsorption kinetics as Lagergren's law is described by the following equation (Eq. 4):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

This can be integrated for the boundary conditions t= 0 to t= t and q_t= 0 to q_t= q_e with q_t equal to the adsorbed quantity at t and q_e the maximum adsorbed quantity in mg g^{-1} of dry biomass. Equation 3 may then be arranged for linearized data plotting as shown by Eq. 5:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{5}$$

Linear Lagergren fits are plotted in Fig. 7. In our case, q_t and q_e are represented by $R_{dm}^{[vns/bio(i)]}{}_t$ and $R_{dm}^{[vns/bio(i)]}{}_{eq}$, respectively. Correlation coefficient values were between 0.6437 and 0.9598, indicating that this pseudo-first order rate expression could not properly fit the experimental data, particularly for Msc. Equation 5 can also be arranged to simulate the adsorption extent q_t at different times with the following equation (Eq. 6):

$$q_t = q_e - 10^{\left(\log(q_e) - \frac{k_1}{2.303}t\right)} \tag{6}$$

When tracing the experimental and modeled adsorption (see Fig.7), it can be seen that the overall adsorption process for longer times is reasonable, whereas the prediction quality for small times is poor. It seems then that the initial adsorption velocity is fast and slows down afterwards.
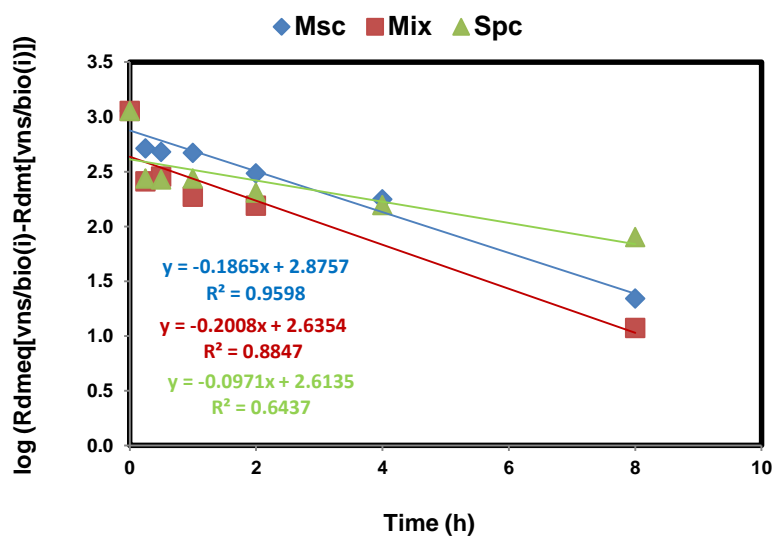
(a)
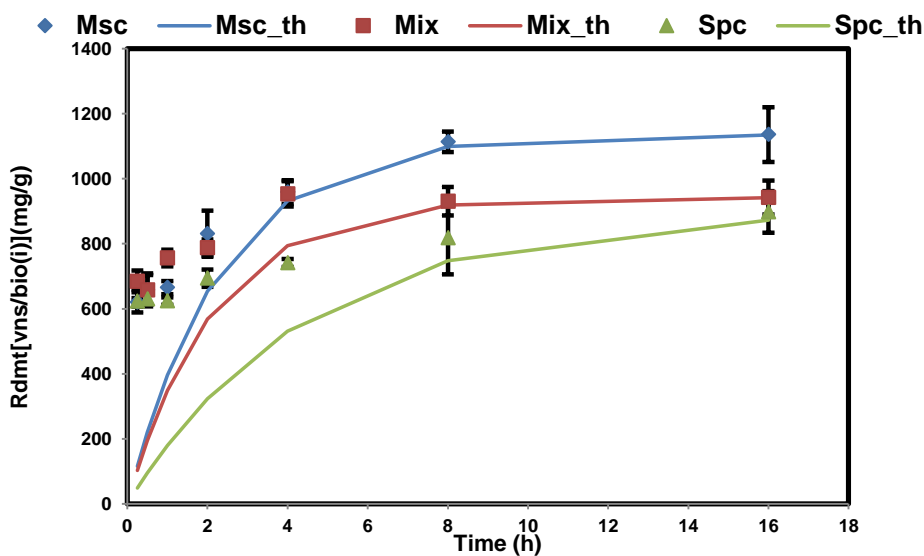
(b)

Fig. 7. Lagergren pseudo-first order model (a: experimental Eq. 5; b: modelled Eq. 6)

Second order kinetic is described by the following equation (7):

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t \right)^2 \tag{7}$$

Integration for the boundary conditions $t= 0$ to $t= t$ and $q_t= 0$ to $q_t= q_e$ leads to Eq. 8:

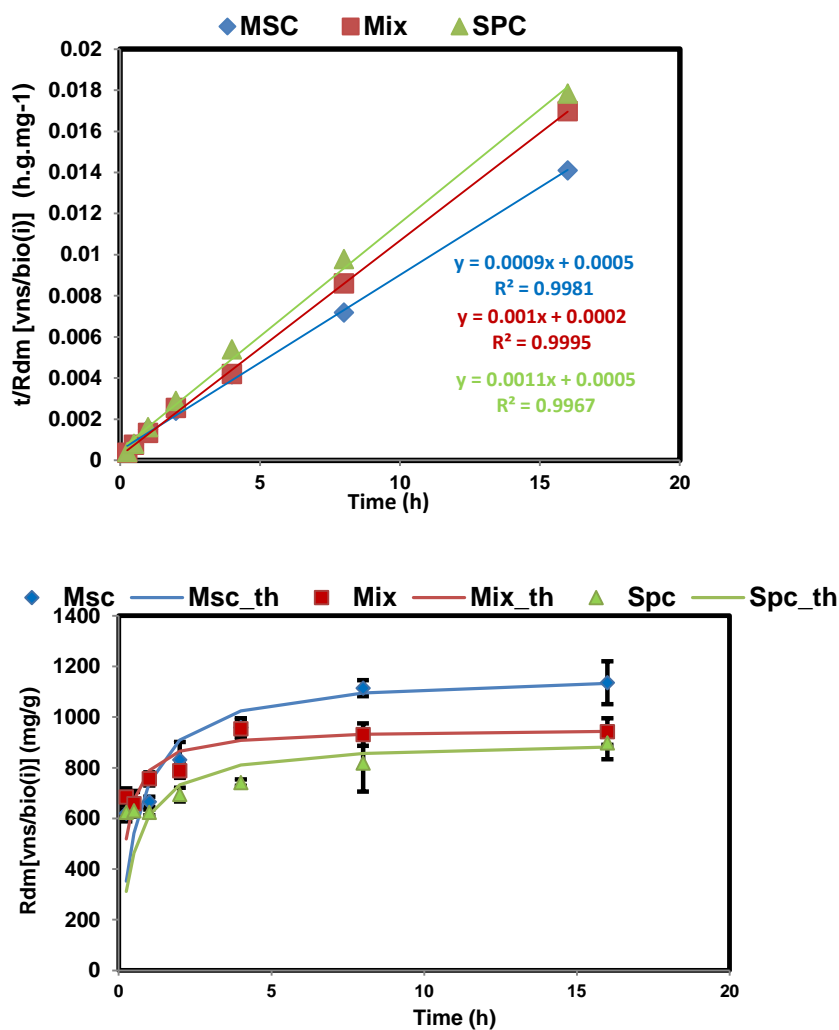$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{8}$$

Equation 8 may then be arranged for linearized data plotting as shown by Eq. 9:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{9}$$

To calculate adsorbance as a function of time, Eq. 8 can be arranged as Eq. 10:

$$q_t = q_e - \frac{1}{1/q_e + k_2 t} \qquad (10)$$

In our case, q_t and q_e are represented by $R_{dm}^{[vns/bio(i)]}{}_t$ and $R_{dm}^{[vns/bio(i)]}{}_{eq}$, respectively. Pseudo second order kinetics fit are given in Fig. 8.

(a)

(b)

Fig. 8. Pseudo-second order model (a: experimental Eq. 8; b: modelled Eq. 9)

The values of the coefficients of determination obtained for these fits were between 0.9967 and 0.9995, indicating that the pseudo-second order rate expression could properly fit the experimental data. This model assumes that the rate-limiting step may be described by complex interactions between sorbent and sorbate. As described in the Hubbe *et al.* reviews, adsorption mechanisms introduce large possibilities of correlations to functional groups of the sorbent (Hubbe *et al*. 2012, 2014). Our data shows then the same tendency observed by Ho and McKay (Ho and McKay 1999): pseudo first-order kinetics in the first 20 min tends to show higher sorption rates than are observed afterwards and fits the whole dataset well, whatever the time. This suggests that the presented sorption system could not be properly described by first-order kinetics and that pseudo-second order kinetics should be used. A main advantage of this model is that the equilibrium capacity and the initial

sorption rate can be obtained from the model (Ho 2006). The sorption capacity may be proportional to the number of active sites occupied by the sorbent (Ho and Chiang 2001). Comparable results have been obtained by Atun and Sismanoglu (1996). In contrast to Ho, they used two pseudo first-order reaction steps and explained that the sorption was mainly controlled by either film diffusion or intra-particle diffusion.

The plotting of experimental data allows for the determination of k_2, $R_{dm}^{[vns//bio(i)]}{}_{eq}$, and half reaction time. Values are given in Table 4.

Table 4. Kinetic Parameters of Pseudo-second Order Model

	Msc	Mix	Spc
R^2	0.9981	0.9995	0.9967
$R_{dm}^{[vns/bio(i)]}{}_{eq}$ $(mg.g^{-1})$	1175	956	908
k_2	1.45E-03	4.97E-03	2.30E-03
Half reaction time (h)	0.585	0.210	0.479

If kinetic data are well-documented in the literature, they mainly concern organic molecules such as dyes, polyphenols, or heavy metal removals on various biomass supports. Modelling of wastewater adsorption was studied by Figaro but on activated carbon, a well-known adsorbent (Figaro *et al*. 2006; Figaro *et al*. 2009). Though experimental data obtained under the same conditions as this study are not found in the literature for comparison, the kinetic constant k_2 and the half reaction time in Table 4 are in the same order of magnitude of the values for the adsorption of molasses wastewaters after anaerobic digestion and melanoidin on activated carbon at pH= 7 (a pH very close to that of vinasse) (Figaro *et al*. 2009). As previously observed during the experiments, Msc presents the maximal adsorption capacity compared to woodchips of Mix and Spc.

The intra-particle model described by Weber and Morris was also tested (Weber and Morris 1962). The rate limiting steps of the adsorption, *i.e*., either external mass transfer (film diffusion), intra-particle diffusion (pore diffusion), or both principally control the process, and the same can be predicted by diffusion coefficients calculated from a diffusion model. The linear form of the Morris-Weber equation (Eq. 11) can confirm the presence or absence of intra-particle diffusion,

$$q_t = k_{id} * t^{1/2} + C \tag{11}$$

where q_t (mg g^{-1}) is the dry matter of vinasse uptake amount at time t (min), k_{id} is the intra-particle diffusion rate constant (mg g^{-1} min$^{-1/2}$), and C is the constant indicating the thickness of the boundary layer. The plot of qt versus $t^{1/2}$ shows multi-linearity indicating three steps that take place:

- Step 1 is the sharper portion taking place at the beginning of adsorption ($t^{1/2}$ lower than 0.5) and may be attributed to the diffusion of the adsorbate in the boundary layer (external diffusion);

- Step 2 describes the intra-particle diffusion taking place between 0.5 and 2.5 h$^{1/2}$; and

- Step 3 is attributed to the final equilibrium stage for which saturation takes place for longer times and where the intra-particle diffusion is rate limited.

In this study, q_t was assumed to be $R_{dm}^{[vns/bio(i)]}$. The coefficient k_{id} can be determined from the slope and C from the intercept of the plot of q_t versus $t^{1/2}$ as shown in Fig. 9.
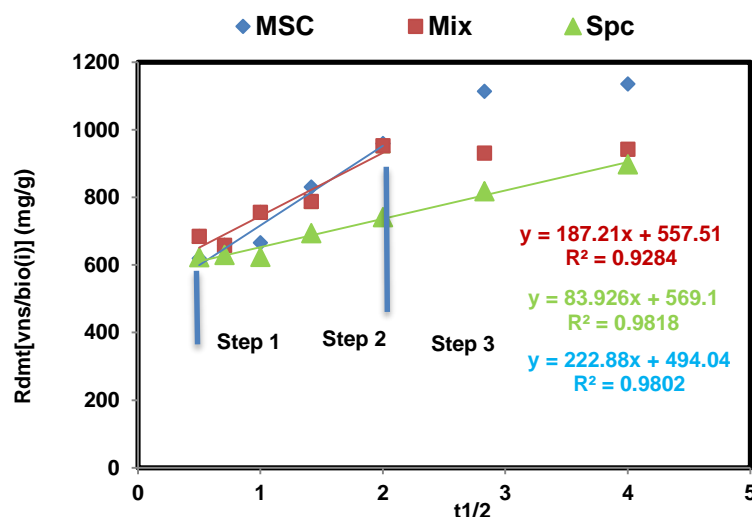
Fig. 9. Intra-particle diffusion model

Coefficient of determination values for Step 2 were 0.92, 0.98, and 0.98 for Mix, Msc, and Spc, respectively. This indicates that the model could reasonably fit the experimental data with the presence of intra-particle diffusion of the vinasse in wood chips as Mix and Msc. The correlation for Step 3 was not calculated due to the small number of experiments in that range. On the contrary, for Spc, Step 3 was not observed. In the time range 0.25 h to 16 h, a dependency of the observed rate on intra-particle diffusion of vinasse was still evident.

CONCLUSIONS

1. These studies at laboratory scale made it possible to distinguish what parameters influence vinasse adsorption on biomass. Effluent dilution had only weak effects on dry matter adsorption, and vinasse adsorption seemed to be mostly a surface phenomenon.

2. The best results were obtained when the biomass surface was considered. These studies also highlighted the different adsorption capacities according to the used wood material, closely linked to biomass structure, available macro-porosity, and surface roughness. Due to its fine and honeycomb-shaped structure, Msc straw was judged to be the best support.

3. Heating the vinasse significantly reduces its viscosity and improves the portion of dry matter of vinasse in dry biomass. The maximal mass transfer in the boundary layer of the adsorbate is obtained for a temperature of 50 °C for a vinasse viscosity of 20 mPas.

4. The pseudo second order kinetic model fit well with the experimental data. Between 0.25 h and 4 h, the intra-particle diffusion of the vinasse was shown to account for

the rate of adsorption for all wood samples. The external diffusion in the solution was the limiting phenomenon for times below 0.25 h, while saturation was observed for two wood samples (Msc and Mix) at times exceeding 4 h. A pseudo first order kinetic model was able to describe adsorption phenomena for long interaction times but failed for short times ranging from 0.5 h to 4 h.

REFERENCES CITED

Akhtar, M., Hasany, S. M., Bhanger, M. I., and Iqbal, S. (2007). "Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions," *Chemosphere* 66, 1829-1838. DOI: 10.1016/j.chemosphere.2006.09.006

Atun, G., and Sismanoglu, T. (1996). "Adsorption of 4,4' -iso propylidene diphenol and diphenylolpropane 4,4' dioxyaceticacid from aqueous solution on kaolinite," *Journal of Environmental Science and Health Part A: Environmental Science and Engineering and Toxicology 31*, 2055-2069. DOI: 10.1080/10934529609376474

Aziz, A. S. A., Manaf, L. A., Man, H. C., and Kumar, N. S. (2014). "Kinetic modeling and isotherm studies for copper (II) adsorption onto palm oil boiler mill fly ash (POFA) as natural low-cost adsorbent," *BioResources* 9 (1), 336-356.

Babel, S., and Kurniawan, T. A. (2003). "Low-cost adsorbents for heavy metals uptake from contaminated water: A review," *Hazardous Materials* 97, 219-243. DOI: 10.1016/S0304-3894(02)00263-7

Caqueret, V., Bostyn, S., Cagnon, B., and Fauduet, H. (2008). "Purification of sugar beet vinasse. Adsorption of polyphenolic and dark compounds on different commercial activated carbons," *Bioresource Technology* 99, 5814-5821. DOI: 10.1016/j.biortech.2007.10.009

Carrocci, J. S., Mori, R. Y., Cobra Guimaraes, O. L., dos Santos Salazar, R. F., de Oliveira, M. F., de Castro Peixoto, A. L., and Izario, H. J. (2012). "Application of heterogenous catalysis with TiO₂ photo irradied by sunlight and later activated sludge system for the reduction of vinasse organic load," *Engineering* 4, 746-760. DOI: 10.4236/eng.2012.411096

Chouchene, A., Jeguirim, M., Favre-Reguillon, A., Trouvé, G., Le Buzit, G., Khiari, B., and Zagrouba, F. (2012). "Energetic valorisation of olive mill wastewater impregnated on low cost absorbent: sawdust versus olive solid waste," *Energy* 39, 74-81. DOI: 10.1016/j.energy.2011.03.044

Christofoletti, C. A., Escher, J. P., Correia, J. E., Urbano Marhino, J. F., and Fontanetti, C. S. (2013). "Surgarcane vinasse: Environmental implications of its use," *Waste Management* 33, 2752-2761. DOI: 10.1016/j.wasman.2013.09.005

Demirbas, A. (2008). "Heavy metal adsorption onto agro-based waste materials: A review," *Journal of Hazardous Materials* 157 (2-3), 220-229. DOI: 10.1016/j.jhazmat.2008.01.024

España-Gamboa, E., Mijangos-Cortes, J., Barahona-Perez, L., Dominguez-Maldonado, J., Hernández-Zarate, G., and Alzate-Gaviria, L. (2011). "Vinasses: Characterization and treatments," *Waste Management and Resource* 29, 1235-50. DOI: 10.1177/0734242X10387313

Figaro, S., Louisy-Louis, S., Lambert, J., Ehrhardt, J. J., Ouesanga, A., and Gaspard, S. (2006). "Adsorption studies of recalcitrant compounds of molasses spentwash on activated carbons," *Water Research* 40, 3456-3466. DOI: 10.1016/j.watres.2006.07.037

Figaro, S., Avril, J. P., Brouers, F., Ouensanga, A., and Gaspard, S. (2009). "Adsorption studies of molasses wasters on activated carbons: Modelling with a new fractal kinetic equation and evaluation of kinetic models," *Journal of Hazardous Materials* 161, 649-656. DOI: 10.1016/j.jhazmat.2008.04.006

Gundogdu, A., Ozdes, D., Duran, C., Bulut, V. N., Soylak, M., and Senturk, H. B. (2009). "Biosorption of Pb(II) ions from aqueous solution by pine bark (*Pinus brutia* Ten.)," *Chemical Engineering Journal* 153, 62-69. DOI: 10.1016/j.cej.2009.06.017

Ho, Y. S. and Mac Kay G. (1999), "Pseudo-second order model for sorption processes", *Process Biochemistry* 34, 451-465. DOI: 10.1016/S0032-9592(98)00112-5

Ho, Y. S. and Chiang, C.C. (2001). "Sorption studies of acid dyes by mixed sorbents". *Adsorption* 7, 139-147. DOI: 10.1023/A:1011652224816

Ho, Y. S. (2006) "Review of second-order models for adsorption sytems" *Journal of Hazardous Materials 136*, 681-689. DOI: 10.1016/j.jhazmat.2005.12.043

Hubbe, M. A., Hasan, S. H., and Ducoste, J. J. (2011). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals," *BioResources* 6(2), 2161-2287.

Hubbe, M. A., Beck, K. R., O'Neal, W. G., and Sharma, Y. C. (2012). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. Part 2. Dye," *BioResources* 7(2), 2592-2687.

Hubbe, M. A., Park, J., and Park, S. (2014). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. Part 4. Dissolved petrochemical compounds," *BioResources* 9(4), 1-144.

Jeguirim, M., Dorge, S., and Trouvé, G. (2010). "Thermogravimetric analysis and emission characteristics of two energy crops in air atmosphere: *Arundo donax* and *Miscanthus giganthus*," *Bioresource Technology* 101, 788-793. DOI: 10.1016/j.biortech.2009.05.063

Johansson, L. S., Tullin, C., Leckner, B., and Sjövall, P. (2005). "Particle emissions from biomass combustion in small combustors," *Biomass and Bioenergy* 25, 435-446. DOI: 10.1016/S0961-9534(03)00036-9

Koppejan, J., and Van Loo S. (2008). *The Handbook of Biomass Combustion and Co-firing*, Earthscan, London.

Lewandowski, I., Kirchenert, A., and Vonie, P. (1995). "CO2-balance for the cultivation and combustion of miscanthus," *Biomass and Bioenergy* 8, 81-90. DOI: 10.1016/0961-9534(95)00008-U

Lisowski, A., Swietochowski, A., Szulc, K., and Lenart, A. (2011). "Density and porosity of the cut and ground material of energy plants," *Agricultural Forest and Engineering* 58, 21-28.

Mohan, D., and Pittman Jr., C. U. (2006). "Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water," *Hazardous Materials* 137, 762-811. DOI: 10.1016/j.jhazmat.2006.06.060

Naiya, T. K., Chowdhury, P., Bhattacharya, A. K., and Das, S. K. (2009). "Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions," *Chemical Engineering Journal* 148, 68-79. DOI: 10.1016/j.cej.2008.08.002

Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Zhang, J., Liang, S., Yue, Q. Y., Li, Q., and Nguyen, T. V. (2013). "Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater," *Bioresource Technology* 148, 574-585. DOI: 10.1016/j.biortech.2013.08.124

Noreen, S., Bhatti, H. N., Nausheen, S., Sadaf, S., and Ashfaq, M. (2013). "Batch and fixed bed adsorption study for the removal of Drimarine Black CL-B dye from

aqueous solution using a lignocellulosic waste: A cost affective adsorbent," *Industrial Crops and Products* 50, 568-579. DOI: 10.1016/j.ind.crop.2013.07.065

Qasim, W., and Mane A. V. (2013). "Characterization and treatment of selected food industrial effluents by coagulation and adsorption techniques," *Water Resources and Industry* 4, 1-12. DOI: 10.1016/j.wri.2013.09.005

Rao, M. M., Ramesh, A., Rao, G. P.C., and Szshaiah, K. (2006). "Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba Pentandra* hulls," *Journal of Hazardous Materials* 129(1-3), 123-129. DOI: 10.1016/j.jhazmat.2005.08.018

Reddy, D. H. K., Seshaiah, K., Reddy, A. V. R., Rao, M. M., and Wang, M. C. (2010) "Biosorption of Pb^{2+} from aqueous solutions by *Moringa oleifera* bark: Equilibrium and kinetic studies" *Hazardous Materials* 174, 831-838. DOI: 10.1016/j.jhazmat.2009.09.128

Robertiello, A. (1982). "Updgrading of agricultural and agro-industrial wastes: The treatment of distillery effluents (vinasses) in Italy," *Agricultural Wastes* 4, 387-395.

Senneca, O. (2007). "Kinetics of pyrolysis, combustion and gasification of three biomass fuels," *Fuel Processing Technology* 88, 87-97. DOI: 10.1016/j.fuproc.2006.09.002

Senneca, O., Chirone, R., Salatino, P., and Nappi, L. (2007). "Patterns and kinetics of pyrolysis of tobacco under inert and oxidative conditions," *Analytical and Applied Pyrolysis* 79, 227-33. DOI: 10.1016/j.jaap.2006.12.011

Shin, E. W., Karthikeyan, K. G., and Tshabalala, M. A. (2007). "Adsorption mechanism of cadmium on juniper bark and wood," *Bioresource Technology* 98, 588-594. DOI: 10.1016/j.biortech.2006.02.024

Sud, D., Mahajan, G., and Kaur, M. P. (2008). "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review," *Bioresource Technology* 99, 6017-6027. DOI: 10.1016/j.biortech.2007.11.064

Vaccari, G., Tamburini, E., Sgualdino, G., Urbaniec, K., Klemes, J. (2005). "Overview of the environmental problems in beet sugar processing: possible solutions", *Journal of Cleaner Production* 13, 499-507. DOI: 10.1016/j.jclepro.2003.09.008

Verma, V. K., Brama, S., Delattin, F., Laha, P., Vandendael, I., Hubin, A., and De Ruyck, J. (2012). "Agro-pellets for domestic heating boilers: Standard laboratory and real life performance," *Applied Energy* 90, 17-23. DOI: 10.1016/j.apenergy.2010.12.079

Weber, W. J., and Morris, J. C. (1962). *Proceedings of the International Conference on water Pollution Symposium*, Pergamon Press, 2, 231-266.

Yadav, A. K., Abbassi, R. Gupta, A., and Dadashzadeh, M. (2013). "Removal of fluoride from aqueous solution and groundwater by wheat straw, sawdust and activated bagasse carbon of sugarcane," *Ecological Engineering* 52, 211-218. DOI:10.1016/j.ecoleng.2012.12.069

Yang, H., and Li, S. (2013). "Energy analysis of cassava vinasse treatment," *Process Safety and Environmental Protection 91*, 503-507. DOI: 10.1016/j.psep.2013.01.003

Yu, L. J., Shukla, S. S., Dorris, K. L., Shukla, A., and Margrave, J. (2003) "Adsorption of chromium from aqueous solutions by maple sawdust," *Hazardous Materials* 100, 53-63. DOI: 10.1016/S0304-3894(03)00008-6