EVALUATION OF HEAVY METAL REMOVAL BY OXIDISED LIGNINS IN ACID MEDIA FROM VARIOUS SOURCES

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The capacity for removal of heavy metals from liquid streams by formation of complexes with lignins oxidized by acid treatment was studied. Lignins were obtained from different sources: sulfuric acid pre-treated cane bagasse, soda pulping bagasse, eucalypt Kraft lignin, and commercial Kraft lignin. These lignins were characterized using different techniques to determine Klason lignin, carbohydrates, total acids, ashes, and their main functional groups: phenolic-OH, carbonyls, etc. The studied lignins were determined spectroscopically using FTIR. In order to increase the metal adsorption capacity, lignins were oxidized at 100°C during 2 h, using aqueous solutions of H_2O_2 in distilled water solvent and HCl catalyst. Some lignin adsorption isotherms were constructed before and after the oxidation process to define Cd(II) ion removal capacity.

Keywords: Adsorption Isotherms; Lignin oxidation; Bagasse lignin; Kraft lignin; Lignin characterization

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INTRODUCTION

After cellulose, lignin is the second most abundant macropolymer in nature (Fengel 1984; Hu 2002). Found in plants, it typically constitutes between 15 and 30% of their mass. Lignin is a three-dimensional amorphous polymer of high molecular weight, being predominantly aromatic (polyphenolic) in character, and is derived from a biosynthetic process in which the main precursors are *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol; these basic units are linked by multitudes of bonds, including ether and carbon-carbon bonds, which form highly complex structures specific to different plant species (Sanjuan 1997). Lignins obtained in the paper manufacturing process are called "technical lignins," of which two types are recognized: commercial or conventional lignins, characterized principally by the presence of sulphur in their makeup, including Kraft lignin and the lignosulphonates; and lignins without sulphur, which are obtained from the soda and organosolv pulping processes (Macorra 2004).

Theory of the adsorption process is widely known, as is its associated technology (Slejko 1985). Adsorption is one of the most useful processes for the removal of metals ions in liquid waste currents from both technical and economic standpoints. Metal ion adsorption on lignocellulosic materials, as well as the activated carbon obtained from them, is considered an alternative to biological and traditional chemical treatments. Studies carried out in packing towers and agitation tanks have found that metals ions such as Pb, Cu, Zn, Cr, Fe, Ni, and Cd, among others, can be removed with efficiencies between 50 and 100%, and that the absorbent materials used performed at least as well, and frequently better, than commercial activated carbon (Basso et al 2002; Dupont et al 2003; Herrera 2005; Lalvani et al 2000). The metal adsorption capacity of a lignocellulosic material is due to lignin surfaces that contain two main types of acid sites, attributed to carboxylic- and phenolic-type surface groups. Such groups have a high affinity for metal ions (Guo et al. 2008).

Oxidation is a method of depolymerization of lignin, used in delignification and cellulose bleaching. Oxidation can be implemented in either acid or alkaline media. During oxidation, phenolic groups are transformed to aldehydes, aromatic carbonyls, and carboxylic groups when the rupture of the aromatic ring occurs (Gonçalves et al 2001; Sarkanen et al 1971).

Studies of cobalt-catalysed lignin oxidation in acidic media have been carried out (Gómez-Pineda et al. 1997). Increasing oxygen content increases the adsorption capacity of lignin due to high electron density groups in the molecule (Gonçalves et al. 2001). The capacity of the lignin to absorb metal and dye was evaluated (Gómez-Pineda et al. 1997; Gonçalves et al. 1997) showing a 5% increases of the adsorption compared with the original lignins.

Infra-red (IR) spectroscopy has been widely used for the characterization of lignins and lignocellulosic materials (Cotrim et al. 1999; Gonçalves et al. 2008). Identification of minor differences in lignin spectra by means of direct comparison and analysis is a very hard task. Lignin spectra present too many overlapped bands, whose intensities depend not only on the origin but also on the isolation method. Multivariate regression analysis can be used to group lignins into classes according to the pulping process and to the post-treatment based on the input of absorbances at certain wavelengths in the IR spectra (Cotrim et al. 1999; Labat et al. 2008). By means of principal component analysis (PCA), for example, a large amount of information contained in a spectrum can be reduced to a few parameters (principal components), for which similar spectra (samples) will give similar scores. In practice, when the scores of the principal components are plotted, similar samples lie close to one another, allowing the qualitative recognition of different groups of samples.

EXPERIMENTAL

Materials

The lignins studied were obtained from differing processes: lignin from sugar cane bagasse soda pulping (BL), lignin from acid pretreated sugar cane bagasse soda pulping (PBL), lignin from eucalyptus kraft pulping (EKL), and Lignotech Ibérica kraft lignin (LKL). Lignins were not submitted to any kind of purification.

Acid Hydrolysis and Klason Lignin

Approximately 2 g of lignin of known moisture content was put in contact with 10 mL sulphuric acid 72% w/w and stirred constantly in a thermostatic bath at 45°C ± 0.5°C for 7 minutes. The reaction was interrupted by the addition of 50 mL distilled water. The sample was then transferred to an Erlenmeyer flask for quantitative analysis, with the addition of a further 225 mL of distilled water. To complete hydrolysis of remaining oligomers, the Erlenmeyer flask was covered with aluminium foil and placed in an autoclave at 121°C for 30 minutes. The resulting suspension was cooled to room temperature and filtered through a filter funnel fitted with rapid filtration paper. The solid was dried to constant weight at 105°C and determined gravimetrically as insoluble lignin (Klason lignin). The resulting filtrate was placed in a volumetric flask and made up to 500 mL with distilled water; samples of the filtrate were used to determine quantities of acid-soluble lignin and carbohydrates (glucans and xylans). The pH of the hydrolysate was adjusted to 1–3 with 6.5 N NaOH, filtered in a Sep-Pak C18 cartridge, and analyzed by high-performance liquid chromatography in a Shimadzu LC10 chromatograph with an Aminex HPX-87H column at 45°C. The mobile phase was 0.01 N H_2SO_4 at $0.6 mL*min^{-1}$.

Ash

Approximately 2 g of lignin of known moisture content was weighed in a porcelain crucible, which had been previously calcined at 800°C, and weighed. Lignin was initially incinerated at 300°C for one hour and at 800°C for another 2 hours. The crucible was then cooled and weighed.

Elemental Analysis

Elemental analysis of lignin was carried out at the Institute of Chemistry of São Paulo University at São Carlos. Analysis was performed in a Perkin Elmer device (Elemental Analyser 2400 CHN), and the results were used to calculate the lignin C_9 formulae.

Total Acid Determination

The method was reported by Silva (1995). The total acids groups, comprising both phenolic and carboxyl groups, were determinate with a titration method. 0.3 g of lignin was mixed with 30 mL sodium bicarbonate 0.1 N for 30 minutes with constant stirring. The mixture was then filtered, and residual sodium bicarbonate was titrated potentiometrically with 0.1 N hydrochloric acid. Equivalent volume was determined by plotting pH against titration volume. The procedure was repeated in the absence of lignin to establish a control.

Total Hydroxyls

In a stoppered test tube 0.03 g dry lignin was mixed with 0.24 mL reagent (pyridine/acetic anhydride 10:3); the reagent had previously been bubbled with nitrogen for 10 minutes (Silva 1995). The mixture was placed in a heater overnight at 65°C, after which the mixture was transferred to an Erlenmeyer flask after adding 15 mL acetone and 15 mL distilled water. The mixture was then left for 1 hour to assure the destruction of any residual acetic anhydride. Acetic acid formed in the reaction was titrated against a standard solution of 0.1 N NaOH with phenolphthalein indicator. The procedure was repeated in the absence of lignin to establish a control.

Phenolic Hydroxyls

Hydroxyl groups were measured using the spectroscopic method described by Wexler (Wexler 1964) and the conductimentric method of Sarkanen and Schverch (Sarkanen et al 1971):

Conductimetric method

Between 0.2 and 0.3 g lignin were suspended in 10 mL ethanol and submitted to magnetic agitation; then 5 mL acetone and 15 mL destilled water were added, causing a fine lignin suspension. The suspension was bubbled with nitrogen for 5 minutes and titrated with 0.1 N LiOH. Equivalent volume was determined by plotting conductivity against titrated volume.

Spectroscopic method

Approximately 0.2 g lignin of known moisture content was dissolved in 50 mL dioxane (96%) and the solution diluted in 1:10 proportion of dioxane and water 1:1 and adjusted to pH 13 by addition of 1 N NaOH. A control was prepared with the same dilution but with pH adjusted to 1 by the addition of 1 N HCl. To calculate percent phenolic OH the median value of lignin models was taken.

Determination of Carbonyl Groups

A spectroscopy method was developed by Alder and Marton in 1966 and reported by Lin (1994). It involves differential absorption measurements that take place when carbonyl groups are reduced at the benzylic alcohol corresponding with sodium borohydride. 2 mL of 0.2 mg/mL lignin solution in dioxane 96% was mixed with 1 mL 0.05M sodium borohydride solution (190 mg in 100 mL NaOH 0.03N). The mixture was left in darkness for 45 hours at ambient temperature and its absorbancy in the 200 – 400 nm band determined against an unreduced lignin solution at the same concentration. The purpose was to distinguish carbonyls groups in two lignin model structures: coniferyl aldehyde (4-hydroxy-3-methoxycinnamaldehyde) and acetoguaiacon (4-hydroxy-3-methoxyacetophenone); the carbonyls groups are located in the aliphatic chain.

Spectroscopic Analysis

Lignin samples for analysis were read for absorbance at 180 and 800 nm in the UV spectrophotometer CINTRA 20. Samples were also analysed by FT-IR spectroscopy in the range of 400 to 4000 cm^{-1} in a Nicolet Avatar 320 FT-IR. Lignin spectra were compared by principal component analysis (PCA) using the software programs BIOTEC and FAEN compiled in FORTRAN (Cotrim et al. 1999; Labat et al. 2008).

Lignin Oxidation

To 100 mL water were added 10 g lignin and 1 mL HCl 2N as a catalyst. The mixture was placed in a 250 mL flask connected to a condenser which generates reflux and heated to boiling, at which time 50 mL hydrogen peroxide 35% solution was added in the form of drops. The reaction was interrupted after 2 hours. Oxidised lignin was filtered and washed with 2 L distilled water to remove acids and residual peroxide. Oxidised lignins were dried in an oven at 65°C.

Sorption Tests

Dosage curves were made for some lignins. Stock solution (1000 mg/L) of Cd(II) ions was prepared in distilled water using cadmium nitrate. Analytical grade reagent was employed. Sorption tests of individual Cd(II) on the lignin samples were performed by contacting weighed amounts of each sample (0.5 to 8 g/L) with 50 mL of the metal solutions of 20 mg/L initial concentrations. Measurements were carried out at pH 6 (Basso 2002). Samples were submitted to inverse agitation for 8 hours; this contact time was long enough to ensure equilibrium attainment (Basso 2002). Unabsorbed metal concentrations were determined through atomic absorption in a PerkinElmer Analyst 800.

RESULTS AND DISCUSSION

Table 1 presents hydrolysis results of the lignins studied. Significant differences were found in lignins, principally in their carbohydrates. BL gave a very high total carbohydrate value of 29.24%, which shows a possible formation of lignin-carbohydrate complex at the time of lignin precipitation, a process that was carried out using sulphuric acid at pH 4. In PBL, total carbohydrates were low, 1.05%, due to the acid pre-treatment used, which hydrolysed the carbohydrates initially present in the cane bagasse before delignification with NaOH.

Table 1. Physico-chemical Lignin Analysis

Component	BL (%)	PBL (%)	EKL (%)	LKL (%)
Klason lignin	66.16 ± 0.40	94.30 ± 0.57	91.63 ± 0.78	89.14 ± 0.42
Soluble lignin	1.60 ± 0.56	1.90 ± 0.03	3.10 ± 0.15	3.11 ± 0.03
Glucans	1.90 ± 0.16	0.69 ± 0.04	0.69 ± 0.001	9.11 ± 0.09
Xylans	27.34 ± 2.83	0.36 ± 0.03	0.47 ± 0.62	2.68 ± 0.20

Alls values are moisture and ash free

LKL showed atypical performance for a lignin; solubility in dioxane was very low, 0.69 g/L, and chromatograms made to assess sugars showed the presence of other components that were hard to classify. The chromatograms also showed the formation of high quantities of formic acid, which must come from lignin degradation and not from existing carbohydrates, which gave an exaggeratedly high figure for total carbohydrates.

The lignins had a high ash content, BL, 5.68%; PBL, 1.72% and LKL, 16.43%; only EKL had ash content with a typical value for Kraft lignin, 0.75%. The ash content in LKL was probably due to copper salt contamination by metal oxidation of equipment in the acid precipitation process.

Table 2 shows results for functional groups. During analysis of these groups, heavy interference was experienced from carbohydrates and ash in the lignins. Only lignins PBL and EKL were soluble in dioxane 96%, and so those were the only ones that could be measured for phenolic OH groups by the Wexler method; values obtained were 1.79% and 2.43% respectively, and were similar to those cited in the literature (Nour-Eddine 2004). It should be noted that there was a great difference in OH values obtained by the spectrophotometric method, which were ten times greater than those from titration with LiOH. LiOH titration was affected by metals ions such as Cu(II) present in the lignin solutions. These ions were a consequence of contamination during the isolation process, which apparently precipitated at the rate the base was added, and sugars, which increased consumption of the base, corresponding in content with measured OH during titration of BL lignin (0.73%), and for LKL (0.39%). These values were much greater than those found for PBL and EKL, which gave values of 0.12% and 0.19%, respectively. Quantification of carbonyl groups was inexact due to interference, probably from metal ions from lignins and the sugars. Results for the presence of carbonyl groups showed that BL lignin had a higher proportion of them, whereas PBL lignin proportions were lower. For LKL lignin it was only possible to present partial results due to the greater interference in generated spectra, yielding results without physical meaning. Calculation of carbonyl group concentration will require the use of more exact techniques, such as NMR spectroscopy.

Table 2. Functional Groups

Functional groups		BL (%)	PBL (%)	EKL (%)	LKL (%)
Total acid		0.11 ± 0.01	0.17 ± 0.01	0.25 ± 0.02	0.008 ± 0.007
Phenolic hydroxyl (cond.)		0.73 ± 0.044	0.12 ± 0.005	0.19 ± 0.04	0.39 ± 0.04
Phenolic hydroxyl (uv)		---	1.79 ± 0.17	2.43 ± 0.21	---
Total hydroxyl		2.02 ± 0.22	1.38 ± 0.48	1.89 ± 0.10	2.62 ± 1.05
Carbonyl	X*	2.34 ± 0.26	0.53 ± 0.15	2.01 ± 0.09	---
	Y*	11.24 ± 0.44	4.99 ± 0.31	5.56 ± 0.18	0.52 ± 0.01

* coniferyl aldehyde structures
** acetoguaiacon structures

A relation appears to exist between functional group concentrations and the possible existence of lignin carbohydrate complexes, as all BL lignin values were higher than those of other lignins, and in second place LKL lignin, which also had higher sugar content than the other two.

Table 3 shows results of elemental analysis carried out on all lignins, together with their C_9 formulae. Carbon values can be seen to be similar for all lignins, and the existence of sulphur was observed in Kraft lignins, incorporated during the pulping process. The presence of nitrogenous compounds in the lignin is somewhat uncommon, and could be related to nitrogenous compounds in plants, such as amino acids or ureas, incorporated into the lignin during the pulping process. Oxidation increased oxygen and decreases hydrogen in the majority of samples, except for LKL lignin, a phenomenon resulting from the reduction in ash quantity (values in Table 3 are free of moisture but not ash), which increases the proportion of each component in the sample. Oxidised lignins are labelled in the following manner: Oxidised BL lignin (BLO), oxidised PBL lignin (PBLO), oxidised LKL lignin (LKLO) and oxidised EKL lignin (EKLO).

To gain further insight into original lignins and the effect of oxidation on them, a principal component analysis was carried out on all lignins, in their original and oxidised states. Figure 1 shows correlations between the various principal components (PC), of which PC1 explained more than 85% of variation between spectra, and PC2 and PC3 close to another 12% of variance. The oxidation process produced a displacement to the right of the scores in the PCA scores analysis.

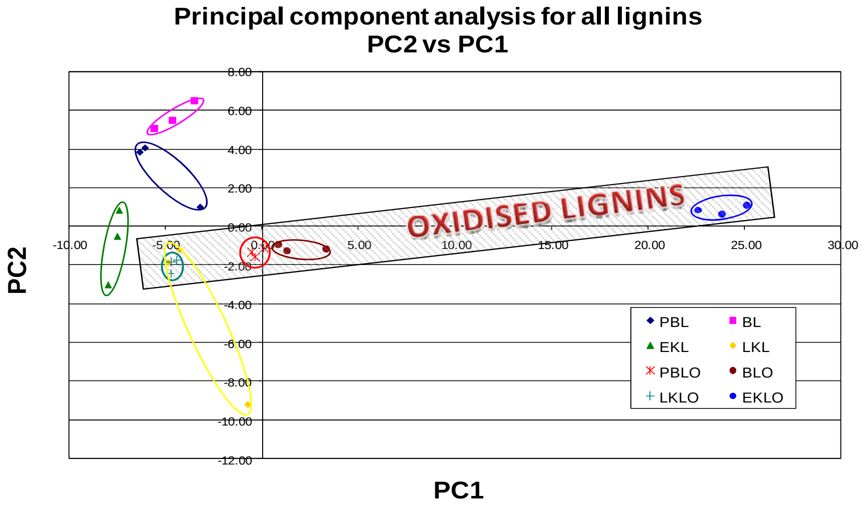
Table 3. C_9 Lignin Formulae

Lignin type	Formulae C_9	Molecular weight
PBL	$C_9H_{10.06}O_{3.945}N_{0.167}$	185.11
PBLO	$C_9H_{9.47}O_{4.44}N_{0.16}$	192.27
U	$C_9H_{10.83}O_{4.96}N_{0.095}S_{0.075}$	202.82
BLO	$C_9H_{8.85}O_{5.35}N_{0.1}S_{0.075}$	207.21
LKL	$C_9H_{9.47}O_{5.06}N_{0.065}S_{0.1}$	203.46
LKLO	$C_9H_{9.05}O_{3.59}N_{0.059}S_{0.067}$	178.16
EKL	$C_9H_9O_{3.45}N_{0.067}S_{0.31}$	183.60
EKLO	$C_9H_{7.92}O_{4.71}N_{0.11}S_{0.82}$	220.16

Analysis of Fig. 1 shows that original lignins were more similar among themselves than with oxidised lignins, and PBLO and LKLO were more similar to the original lignins than the others lignins; lignin EKLO, which underwent more transformation than the others, was found furthest from the original lignins. Lignin LKL was observed to be most different from other original lignins but, when oxidised, the results were superimposed over those of bagasse cane lignin. Spectroscopic analysis showed that differences between lignins was related to the number of unsaturated bonds, the number of carbonyl groups (the main consequence in the oxidation process), and the number of aromatic and OH groups.

Comparing principal component values, changes in lignin functional groups BL and PBL could account for 66% and 40% of the observed changes when the samples were submitted to oxidation. According to the literature (Weneger et al. 1984), the main changes occurring when lignin is oxidised are due to variation in the number of carbonyl groups due to the destruction of aromatic rings and alcohol groups. Subspectra of PCA, Fig. 2, presents different absorption peaks in 1746 cm^{-1}, which correspond to oxygen, ketones, and other carbonyl group absorptions. Due to difficulties in characterization of lignins used, however, NMR analysis will be required to verify changes in lignin structure during oxidation.

Metal ion adsorption tests were made for aqueous phase lignins BL, BLO, PBL, and PBLO. Figure 3 shows dosage curves for Cd(II). The BL had higher Cd(II) removal capacity than the PBL, which is attributed to the higher acid totals and carbonyl groups present in the structure of the lignin; the principal difference was in the content of the carbonyls groups. The oxidation process increased the percentage of Cd(II) removed for both lignins, and the maximum Cd(II) removal percentage was approximately 80%.


Principal component analysis for all lignins
PC2 vs PC1

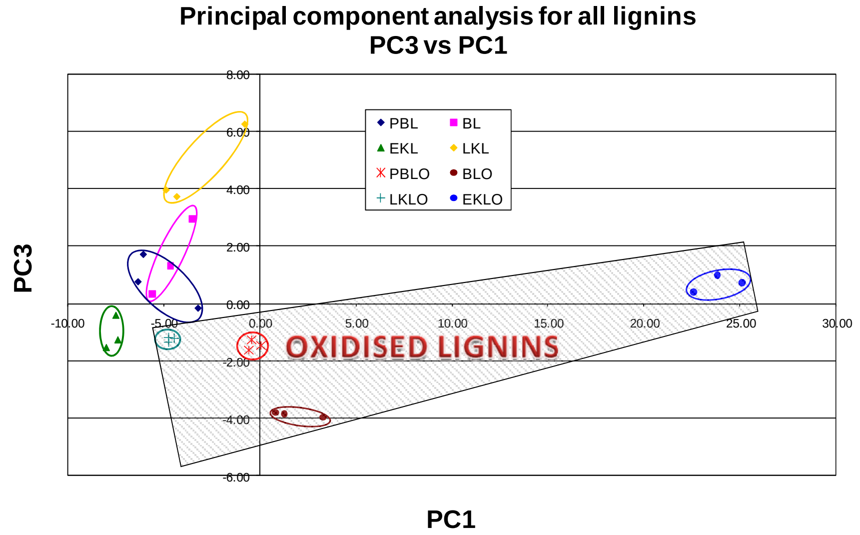

Principal component analysis for all lignins
PC3 vs PC1

Figure 1. Lignin principal component analysis, scores analysis.

CONCLUSIONS

1. The main differences between the lignins investigated in this work were the sugar concentrations and amounts of carbonyls and total hydroxyl groups.
2. BL and PBL were the most similar lignins to each other. These lignins were close in the graphs of correlation of the principal components (PC).
3. Infra-red subsprectra obtained by principal component analysis of the bands present at 1746 cm^{-1} corresponded to absorption of the carbonyls groups.
4. Lignin is capable of adsorbing Cd(II) from aqueous solution. The percentage removal showed a slight increase in adsorption capacity when lignin was oxidised.
5. The oxidation of lignins was corroborated through FT-IR analysis due to increase in a band of carbonyl groups and the right-hand displacement of lignin values in correlation graphs of principal component analysis.

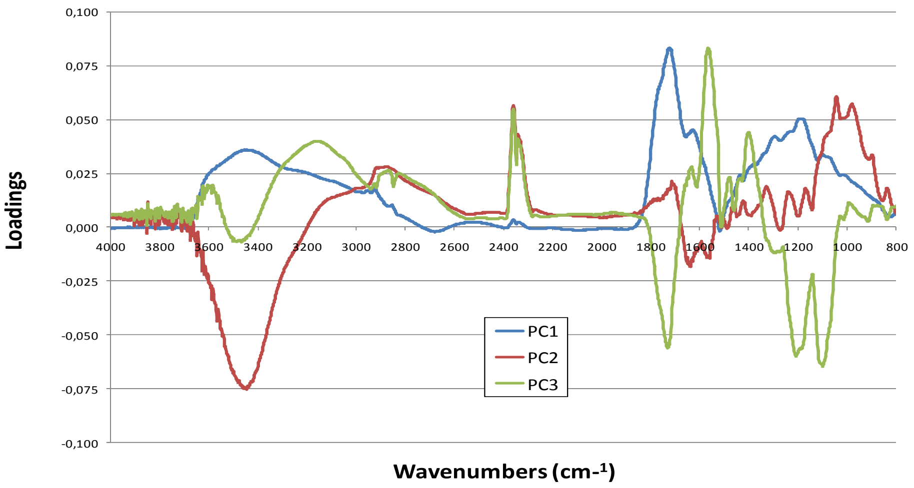


Figure 2. Lignin principal component analysis, PCA subspectra.

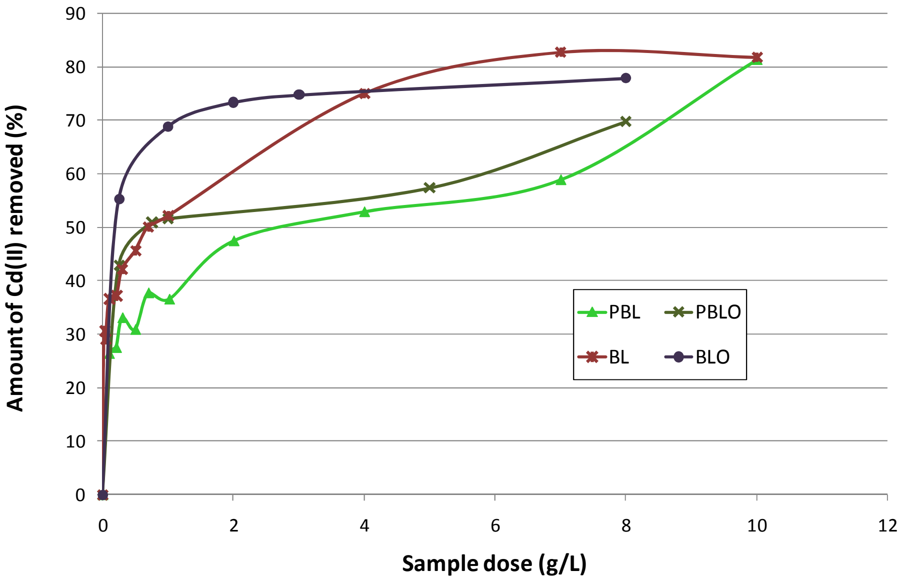


Figure 3. Dosage curves for some BL, PBL, BLO, PBLO.

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