Removal of Lignin from Pulp Waste Water's Black Liquor via By-Pass Cement Dust

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Abstract

The potential use of inexpensive and available by-pass cement dust as an inorganic sorbent for the removal of organic matter (lignin) from black liquor of pulp wastewater by adsorption methodology was investigated using the batch technique. The cement dust is found to remove lignin efficiently from black liquor (the untreated cement dust (70.47%), the thermally treated one at 1000°C (78.63%), and chemically treated dust (80.62%). The factors affecting the uptake percentage such as time, dose, pH and temperature were investigated to assess the optimum conditions for lignin removal.

X-ray patterns were studied to reveal the relationship between the main constituents of each cement dust phase (untreated, thermally and chemically treated) and lignin uptake. By applying Langmuir and Frendlich adsorption isotherms it was found that the adsorption process of lignin from black liquor on by-pass cement dust achieves Frendlich model, which suggests that adsorption is not restricted to one specific layer of sites but involves multi-layers.

Also, stripping of lignin by using different strippers (organic, mineral acids, bases and salts) was investigated. The results obtained show that the organic strippers give high stripping percentage for cyclohexane (90.10%) because lignin is a non-polar compound that dissolves in non-polar solvents. In the case of acids, bases and salts the best results were obtained with much diluted solutions (0.001 mol/L). Stripping of lignin from by-pass cement dust is considered as a way of its recycling for different applications.

Introduction

Lignin is a characteristic chemical component of the tissues of higher plants such as softwoods and hardwoods, where it is typically present in the xylem [1]. Lignin is considered to be a random, amorphous, three-dimensional polymer, which does not posses a uniform and homogenous structure. It is comprised of various types of phenyl propane units possessing a variety of functional groups [2]. Lignins contain several functional chemical groups, such as hydroxyl (phenolic or alcoholic), methoxyl, carbonyl and carboxyl, in various amounts, depending on the origin and the isolation process applied [3,4].

In wheat straw about 15 percent of dry weight is lignin. Straw lignin has a high solubility in alkali solutions [5]. Lignins derived from monocotyl plants (grasses and cereal straw) contain also significant amounts of ρ-coumaryl alcohol residues [6]. The relative amounts of the monolignol units differ considerably between plants. In softwood lignin, the network is formed primarily by coniferyl moieties (95%), the rest consisting of ρ-coumaryl alcohol-type units and only trace amounts of sinapyl alcohol moieties, while in hardwood and dicotyl crops like hemp and flax, various ratios of coniferyl/sinapyl have been reported [6,7].

Lignins from trees, plants and agricultural crops with different chemical composition and properties can be obtained by using several extraction methods. Commercial chemical pulping processes (sulfite and Kraft process) produce lignosulfonates and Kraft lignins as a residue. Commercialized alkaline pulping-precipitation process provides sulphur-free, free-flow-

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ing lignins [8]. Other delignification technologies use a high-pressure steam treatment or organic solvents [9]. However, it is practically impossible to isolate pure lignin quantitatively from cell walls in an intact state.

The lignin isolated by known methods (physical, chemical or enzymatic treatments) is a mixture of degraded or solubilized lignin from various unidentified morphological regions. Lignin is generally obtained as a by-product in the paper production, through the separation from cellulose fibers [10]. Its structure depends on the kind of process used for delignification [11]. Due to its phenolic nature many ways of its chemical modification have been suggested. For example, it has been used as a main chain on which other synthetic polymer chains can be grafted [12]. Due to the presence of phenolic groups in lignin, it is expected that it can increase the oxidation, thermal and light stability of polymeric materials [13].

Lignin has been used as a thermoplastic to obtain new materials. The use of lignin as a stabilizer for plastics and rubbers, where it acts as an antioxidant or modifier of the mechanical properties was reported in refs [14,15]. The blends of lignin with polyvinyl acetate [8], where it improves some mechanical properties, with polyethylene and polypropylene, where it acts as a stabilizer against degradation reactions [13, 14, 16 and 17] with polyvinyl chloride [18] were also reported. A wide quantity of lignin is obtained as a by product of the paper industry and traditionally has been used as a fuel to produce energy [10].

The problem of color removal from pulp-and-paper mill waste has been a subject of serious research in the last few decades. The colorings present in the wastewater from pulp-and-paper mills are organic in nature and comprised of wood extractives, tannins, resins, synthetic dyes, lignin and its degradation products formed by the reaction of chlorine with lignin [19-21]. The discharge of colored pulping effluents to the receiving waters inhibits photosynthetic activity of aquatic biota by reducing the penetration of sunlight. Besides their direct toxic effects on biota [22,23] the color compounds also chelate metal ions and may cause contamination by heavy metals [19]. It is imperative that the color present in pulp-and-paper mill effluents is removed before being discharged into receiving waters. Several physico-chemical color removal methods such as chemical precipitation, rapid sand filtration, membrane processes and adsorption have also been developed [24]. The adsorption of organic compounds and membrane processes were found to be efficient [25].

The most commonly used methods to remove organic substances of low concentration from waste water involve solvent extraction, separation using specific membranes, and adsorbent materials such as activated carbon, porous hydrophobic polymers [26] and clays [27]. Chemical precipitation using alum (aluminum sulfate hydrate), ferric chloride, and lime has been studied [19,28-32] and when clays were used in combination with aluminum sulfate hydrate it resulted in improved color removal due to clay characteristics, as compared to aluminum sulfate hydrate alone [33]. The aim of this work is to develop a novel methodology for removal of lignin from pulp waste water by low cost materials (by-pass cement dust).

Experimental

The black liquor was delivered from Alexandria Paper factory. The structure of lignin in black liquor was investigated by FTIR spectroscopy after its separation as a solid (Fig. 1). The results obtained are in agreement with the data reported by Nilgul and Nihat [34]. The black liquor characteristics are summarized in Table 1. The spectrophotometric determination of lignin in black liquor has been done as follows: 100 ml of black liquor was evaporated in gas suction cupboard to concentrate the residue in solution, 1 g of residue was leached by Kalson method [35] to scrap anything except for lignin when 1 g residue was placed in a beaker, 15 ml of 72% H_2SO_4 were added and the mixture was left for 2 hours, then 560 ml of distilled water was added and refluxed for 4 hours after starting boiling. The precipitate was filtrated and washed with hot water and then dried at 60°C.

From the FTIR spectrum of the studied lignin matter the following groups were detected:

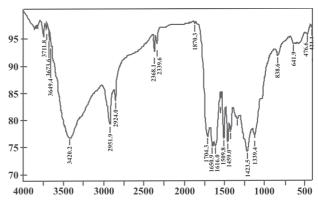a   Broad band at 3420 cm^{-1} due to the hydrogen-bonded OH groups of phenolic and aliphatic structure.

Fig. 1. FTIR spectrum of lignin.

Table 1

Characterization of black liquor

Raw material	Straw
Quantity of black liquor	12 m/tonne of pulp
PH	9-10
Total solids	29658 mg/l
Suspended solids	300 mg/l
COD	9814 mg/l
BOD	30991 mg/l

b Bands at 2924 cm^{-1} and 2851 cm^{-1} arising from C−H stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains that reflects the phenolic nature of lignin.

The spectrophotometric procedure (Fig. 2) was carried out by preparing different concentrations of lignin from stock concentration of 0.005 g lignin which was dissolved in 100 ml of 0.1 N NaOH under open reflux with stirring at 90°C [36]. The selection of the wavelength for the stock sample was performed on double beam UV/VIS Spectrophotometer SHIMAD-ZU model 160A, where the λ_{max} was found at 302 nm. The calibration curve of lignin was obtained using different concentrations with 0.1 N NaOH as a reference solution (Fig. 3).

Materials

By-pass cement dust was delivered from the National Cement Company, Helwan, Cairo, Egypt. The chemical analysis of the untreated, thermally treated at 1000°C, 1050°C, 1100°C, 1150°C and chemically treated by-pass cement dust with 0.01 M HCl are listed in Table 2. X-ray diffraction pattern of by-pass
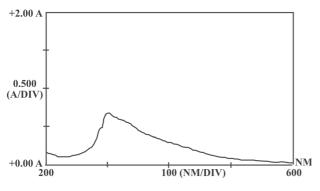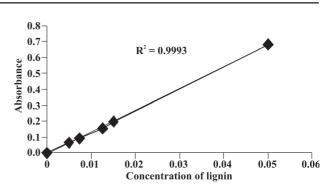
Fig. 3. Calibration curve of lignin material.

cement dust is shown in Fig. 4. It is clear that the main constituents in these materials are calcite $CaCO_3$, quartz, $CaSO_4$, $CaSiO_3$ and NaCl.
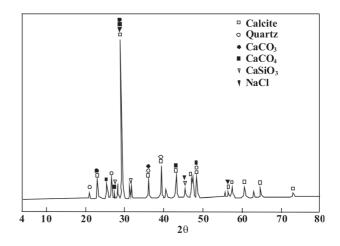
Fig. 4. X-ray diffraction of by-pass cement dust.

The components of by-pass cement dust after thermal treatment are shown in Table 2, and the main constituent in these samples is CaO. After chemical treatment the phases of calcite $CaCO_3$ were predominant. The aim of the treatment of the by-pass cement dust is to study the effect of the phases on the uptake efficiency. X-ray diffraction patterns are shown in Figs. 5 and 6. It is obvious that the main components of the untreated cement dust are α-SiO_2-quatz, calcite $CaCO_3$, $CaSO_4$, $CaSiO_3$, and NaCl. X-ray diffraction patterns of the thermally treated by-pass cement dust at different temperatures ranging from 1000 to 1150°C are shown in Fig. 5.

Comparing X-ray diffraction of the thermally treated by-pass cement dust at 1000°C to untreated by-pass cement dust revealed that calcite $CaCO_3$ was converted to CaO while additional peaks of α-Al_2O_3, γ-Al_2O_3, ω-$3CaO \cdot Al_2O_3$ are clearly observed and the interchange of $2CaO \cdot Al_2O_3$ at 1050°C to $CaO \cdot Al_2O_3$.

Fig. 2. Spectrum of lignin compound.

Table 2
Chemical constituents of untreated, thermally and chemically treated by-pass cement dust

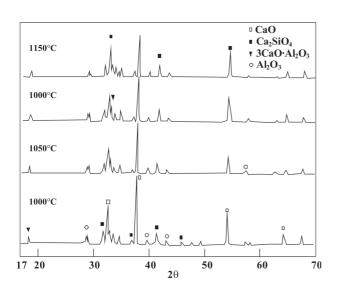| Chemical constituent of cement dust	Untreated cement dust, %	Thermal treated cement dust, %	Chemical treated cement dust, %
CaO	44.24	63.2	32.62
SiO$_2$	10.54	15.05	7.77
MgO	1.45	2.07	1.06
Fe$_2$O$_3$	1.92	2.74	1.41
Na$_2$O	2.00	2.85	1.47
K$_2$O	3.5	5.00	2.58
P$_2$O$_5$	6.35	9.07	4.68
Al$_2$O$_3$	4.7	6.7	3.46
Loss by ignitions	30.00	0.00	29.44

Fig. 5. X-ray diffraction of thermally treated by pass cement dust.

Fig. 6. X-ray diffraction of chemically treated by-pass cement dust by HCl (0.01 mol/L).

·SiO$_2$. The X-ray diffraction of the chemically treated by-pass cement dust is shown in Fig. 6. It is clear that the main constituents are calcite and quartz where the part of weight loss is related to conversion into CaCl$_2$ (15.51%).

Removal Procedure

Before using the black liquor, 1 ml of black liquor was diluted by adding 100 ml of distilled water. 10 ml from diluted black liquor was shaken with by-pass cement dust using a thermostatic shaker water bath at different conditions (contact time, temperature, pH and loading) to remove lignin from black liquor. Then
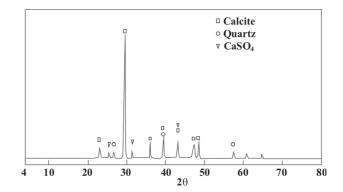
the sample was centrifuged and filtered to determine the remaining amount of lignin. All the experiments were performed in triplicates and the mean values of lignin uptake efficiency were calculated.

The lignin uptake efficiency by by-pass cement dust was calculated according to the following equation:

$$\text{Uptake efficiency} = C_0 - C_w/C_0 \cdot 100\% \quad (1)$$

where C_0 is the initial concentration and C_w is the final concentration.

The stripping efficiency of lignin from cement dust was calculated according to the following equation:

$$\text{Stripping} = C_w/C_0 \cdot 100\% \quad (2)$$

where C_0 is the concentration of lignin in cement dust, and C_w the concentration of lignin present in the stripper.

Results and Discussion

Effect of Contact Time

The effect of contact time on the uptake was studied by shaking 0.05 g of cement dust with 10 ml of diluted black liquor for different times at room temperature. Figure 7 shows that the lignin uptake efficiency is increased as contact time increases until it reaches maximum values of 6.56%, 21.27%, 22.85% and 22.85% at 5, 10, 20 and 30 min, respectively. The optimum time was chosen to be 20 min.
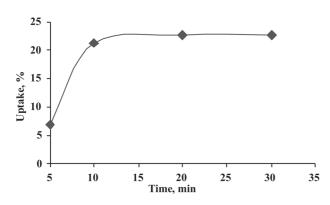

Fig.7. Effect of contact time on the uptake percent of lignin at 10 ml of diluted black liquor, 25°C, 0.05 g by-pass cement dust, liquor pH (9.34).

Effect of Loading Weight

The effect of loading weight on the uptake of lignin was studied by shaking 10 ml of diluted black liquor with different weights of by-pass cement dust from 0.05 g to 2 g at the pH of the liquor, room temperature and 20 min shaking time. Figure 8 shows that the uptake of lignin is increased as loading increases until it reaches the maximum value of 88.04% at 0.9 g. This is due to the increase in surface area caused by increase in weight.
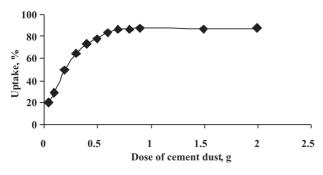

Fig. 8. Effect of loading weight on the uptake percent of lignin at 25°C, liquor pH (9.46) and 20 min.

Effect of Temperature

The effect of temperature on the uptake of lignin was studied by shaking 0.2 g of by-pass cement dust with 10 ml of diluted black liquor under the pH of liquor and 20 min shaking time. The results are shown in Figure 9, from which it is clear that the maximum value was at 60°C as endothermic process proceeds until the formation of a layer on the surface of a solid matrix (cement dust).
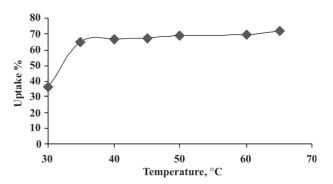

Fig. 9. Effect of temperature on the uptake percent of lignin at liquor pH (9.50), and 0.2 g by-pass cement dust with 20 min shaking time.

Effect of pH Value

pH plays an important role in the adsorption mechanism. The pH of wastewater should be adjusted before treatment with by-pass cement since the black liquor is a mixture of various components that may exhibit some buffering properties and resist the pH adjustment.

pH of solution was fixed at a certain value by buffer solution. The isolated lignin is not a pure lignin but it represents all lignins that contain this structure and phenolic groups. In addition the isolated lignin has a specific peak that appears at 302 nm.

0.2 g from by-pass cement dust was shaken with 10 ml of diluted black liquor at room temperature for 20 min. pH was adjusted as 15 ml diluted black liquor/15 ml Tris buffer or any type of phosphate and thiel buffers were used. Figure 10 shows that the maximum uptake with Tris buffer was 74.27% at pH 7.2 but with thiel buffer it was 58.27% at pH 7.0 and with phosphate buffer it was very low uptake 17.92%.

Effect of Thermally Treated by-pass Cement Dust

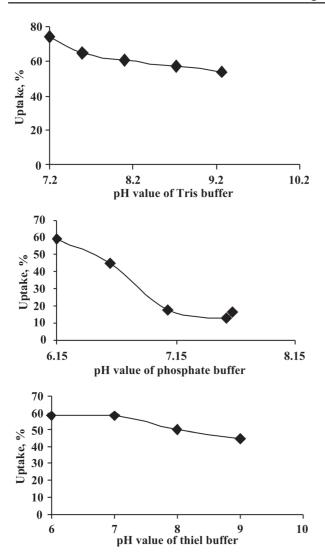Effect of thermally treated by-pass cement dust on adsorption of lignin was studied at the optimum

Fig. 10. Effect of different buffers on the uptake percentage of lignin from black liquor.

conditions, by shaking 10 ml of diluted black liquor with 0.9 g of thermally treated by-pass cement dust at 60°C and pH 7.2 using Tris buffer in thermostatic shaker for 20 min. Figure 11 shows that the increase in temperature the decreases the uptake percentage. The results indicate that the cement dust thermally treated at 1000°C is much more effective than its untreated form because of conversion of calcite $CaCO_3$ into CaO, which acts as a good sorbent for lignin.

Effect of Chemically Treated By-pass Cement Dust

The effect of chemically treated by-pass cement dust on the adsorption of lignin was studied at the optimum conditions, by shaking 10 ml of diluted black liquor with 0.9 g of chemically treated by-pass cement
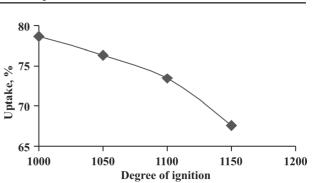

Fig. 11. The relationship between degree of ignition and uptake of lignin from black liquor on by-pass cement dust using 0.9 g of thermally treated by-pass cement dust, 60°C, 20 min at pH 7.02 using Tris buffer.

dust at 60°C and pH 7.2 using Tris buffer in thermostatic shaker for 20 min. The results indicated that the uptake is reaching 80.62% under these conditions.

Adsorption Isotherms

Frendlich model in dilute solution is formulated by the following equations:

$$Q_e = K_f \cdot C_e^{1/n} \qquad (4)$$

$$\log Q_e = \log K_f + 1/n \log C_e \qquad (3)$$

where Q_e is the amount of lignin retained by unit mass of sorbent; C_e is the amount of lignin remaining in solution; and K_f and n are constants.

Figure 12 shows that the adsorption process of lignin on by-pass cement dust fits Frendlich model, which suggests that adsorption is not restricted to one specific layer of sites but to multi-layers. From the slope and the intercept, the Frendlich parameters are calculated, $K_f = 2.39$, $1/n = 2.0983$ and $n = 0.47$. It indicates that lignin is adsorbed on cement dust and forms multi-layers.
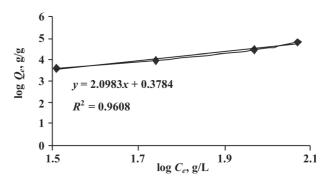

Fig. 12. Frendlich equilibrium isotherm of lignin adsorbed by cement dust.

Stripping of Lignin from By-pass Cement Dust

Stripping of adsorbed lignin from by-pass cement dust may be considered as a possibility for its recycling with subsequent use in different applications. Using different solvents as strippers at 30 min, shaking time and 10 ml of the stripper the results were obtained and summarized in Table 3.

Table3
Selected properties of some organic solvents

Stripper kind	$M_{g/mol}$	μ_D	Stripping, %	Lable
Acetone	58.1	2.69	21.07	1
Ethanol absolute	46.1	1.66	72.37	4
Methanol	32	2.87	86.18	5
Dioxane	---	0	50.67	2
Benzene	78.1	0	90.13	6
Cyclohexane	---	0	92.10	7
Toluene	92.1	0.31	58.56	3

Table 3 shows the properties of some solvents where M is the molar mass, μ is the dipole moment. When $\mu = 0$ it means these are non-polar hydrocarbon compounds, but not all (*e.g.* toluene has $\mu = 0.31D$) are also considered as fully non-polar compounds. As the dipole moment value increases, the polarity and also stripping percentage increases. From the results, we can clearly understand that lignin is a non-polar compound, which dissolves in non-polar solvents, so stripping is efficient in non-polar solvents. However, it was found that cyclohexane stripped 90.10% and this value decreases from benzene, toluene to dioxane (Fig. 12) due to the presence of resonance at benzene ring and also, the presence of CH_3-groups in toluene. In these compounds the electron density is high, so an electric field may be generated from the solvent, which leads to a decrease in stripping percentage. Lignin can also be stripped from by-pass cement dust by using bases and salts (Fig. 13). It was found that HCl gives the maximum value in mineral acids and NaOH gives the maximum value of 90% (Figs. 14, 15).

Conclusions

Application of by-pass cement dust as an adsorbent in the removal of lignin from pulp waste water
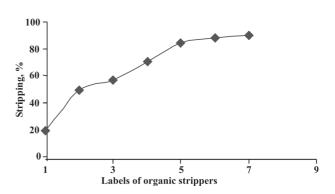

Fig. 13. Stripping of lignin from by-pass cement dust using organic solvents.
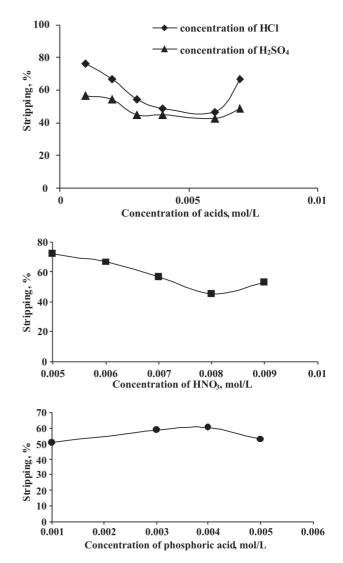

Fig. 14. Stripping of lignin from by-pass cement dust using different mineral acids. at 30min. shaking time and 10 ml from the stripper at room temperature.

shows good results of untreated (70.74%), thermally treated at 1000°C (78.63%) and chemically treated (80.62%) respectively. Under the tested conditions
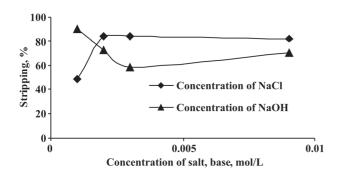
Fig. 15. Stripping of lignin from by-pass cement dust using base as sodium hydroxide and salt as sodium chloride at shaking time 30 min, 10 ml from stripper at room temperature.

of 0.9 g of untreated, thermally or chemically treated cement dust, 10 ml of diluted black liquor and adjusted by Tris buffer to pH 7.2 and shaken for 20 min in thermostatic water bath at 60°C.

The fitting of adsorption process to Frendlich model suggests that adsorption is not restricted to one specific layer but to multi-layers. From the slope and intercept, the Frendlich parameters were calculated, K_f = 2.39, $1/n$ = 2.0983 and n = 0.47. Up to 90.10% of lignin can be stripped from by-pass cement dust by cyclohexane.

Acknowledgment

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