# ADSORPTION OF DIETARY OILS ONTO LIGNIN FOR PROMISING PHARMACEUTICAL AND NUTRITIONAL APPLICATIONS

Rasha Tolba, Guosheng Wu, and Aicheng Chen*

Kraft lignin, a by-product of the pulp and paper industry, was explored as an adsorbent for six dietary oils and was compared to chitosan, which is widely used in the pharmaceutical market. The dissolution and adsorption efficiency of kraft lignin were tested at an acidic pH corresponding to the stomach, as well as at a basic pH corresponding to the intestine. Results showed that kraft lignin is a powerful adsorbent that can take up dietary oils at up to about 6 times its own weight. Kraft lignin exhibits higher stability and insolubility at the pH of the stomach in comparison to chitosan. The adsorption isotherm of dietary oils fits well with the Freundlich model, and the adsorption kinetics follows a pseudo-second order relationship.

*Keywords: Lignin; Vegetable oil; Adsorption; Chitosan; Adsorbent*

*Contact information: Department of Chemistry, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7B 5E1 Canada. * Corresponding author. Tel.: +1 807 343 8318; Fax: +1 807 346 7775; E-mail address: aicheng.chen@lakeheadu.ca*

## INTRODUCTION

Edible oils such as canola oil, olive oil, sunflower oil, corn oil, cottonseed oil, and peanut oil are fixed oils. They are composed primarily of triacylglycerols (TAGs), which are glycerol esters of fatty acids (FAs). These TAGs represent the saponifiable part of vegetable oil, while the main components of unsaponifiables are tocopherols, pigments, trace elements, phospholipids, and sterols, which are present in different amounts in the oil. The saponification value (SAP value) is a unique means of oil identification. It is defined as the weight of potassium hydroxide, in milligrams, required to neutralize the free FAs and to saponify the esterified FAs that are present in one gram of oil or fat. Several methods for the determination of fatty acid content in edible oils have been suggested (Lowry and Tinsley 1976; Chen et al. 1999; Ayorinde et al. 2000). The SAP value for fixed oils ranges from 165 to 250 (Gunstone 2002). Oils compose the major fat component in the human diet, and the digestion of edible oils begins in the small intestine lumen at pH 6 to 8 (Marks et al. 1996).

Oils participate significantly in contributing to obesity, a serious health problem that predisposes one to atherosclerosis, heart disease, stroke, and diabetes. Several approaches have been developed to address the obesity problem, such as restricted caloric diet, regular exercise, antihypercholesterolimic agents, acupuncture, and surgical intervention. However, chemically derived drugs are clearly not the perfect answer due to safety concerns. Hence, safer natural alternatives have to be considered.

Chitosan has been widely available over-the-counter as a natural fat adsorbent and blocking agent for preventing obesity and hypercholesterolemia. It is a natural

polysaccharide that is composed of 1,4-linked glucosamine residues, which are obtained from the N-deacylation of chitin exoskeletons of crustaceans such as shrimp and crab. It has a slightly basic nature in aqueous solution, and it decreases dietary fat absorption by increasing the viscosity of fluids in the intestine, thus inducing a "fullness" effect (Bokura and Kobayashi 2003). Some studies have shown that chitosan is effective in the reduction of serum LDL cholesterol over eight weeks of treatment; however, the lipase inhibitor, Orlistat, was found to be faster and more effective for weight management (Guerciolini et al. 2001). The adsorption of residue oil from palm oil mill effluent (POME) using chitosan has also been investigated, indicating the chemisorption nature between the residue oil and chitosan (Ahmad 2005). On the other hand, it is always a prudent policy to have alternatives for any pharmaceutical product, since this allows physicians to select from a variety of treatment options, some of which may be more convenient and present fewer contra-indications for specific patients, who might experience discomfort when using chitosan. Thus, it is important to study the adsorptive properties of lignin and to explore its application in pharmaceutical formulations for the control of obesity and hypercholesterolemia.

Lignin is an abundant natural compound. It is one of the most essential components of the plant cell wall (Knudsen 1997; Heitner et al. 2010). It exists in plants chiefly as lignocelluloses. The non-starch polysaccharides and lignin that compose the plant cell wall are commonly referred to as dietary film (Aman et al. 1995; Bunzel et al. 2001). Kraft lignin is extracted from wood pulp, and is then purified, washed, and modified for its use in many applications (Tian et al. 2010; Tolba et al. 2010). Lignin has also been used as a marker in digestion studies. The ideal marker must be indigestible and nonabsorbable, thus it does not affect and is not affected by the digestion process. It must also be physically similar to the material that is to be marked, which is estimated by a sensitive and specific method (Fahey and Jung 1983). Many trials report that lignin is an inert, indigestible dietary fiber (Ellis et al. 1964; Forbes et al. 1964; Gray 1975). No known anaerobic microbial or mammalian enzyme has the capacity for degrading lignin (Van Soest 1982). Lignin cannot be attacked by alimentary bacteria, and this is likely due to a certain degree of inherent antiseptic action that originates via its phenolic nucleus (Woodman and Stewart 1932). Significantly high percentages of 99.3% and 97.8% of dietary lignin were recovered in the feces of rabbits and steer, respectively (Crampton and Maynard 1938). These results support the premise that dietary lignin is not metabolized by mammals and that the true digestion of lignin as an energy source has not been proven. On the other hand, some studies have shown that 10% of dietary lignin is digested mainly in the stomach; however, the chemical composition of the lignin that passed through the duodenum closely matched that of fecal lignin (Porter and Singleton 1971). The solubility of lignin in a relatively high concentration of sulphuric acid was reported (Macdonald and Campbell 1952). The stomach enzyme pepsin is active in acidic medium and it has not, as yet, been proven that lignin is soluble in dilute acid at the temperature at which this enzyme is active (Crampton and Maynard 1938).

Lignin has been investigated as an inexpensive natural adsorbent for bile acids, cholesterol, surfactants, and for the removal of toxic matter from wastewater such as phenols, pesticides, dyes and heavy metals (Peternele et al. 1999; Dizhbite et al. 1999; Lalvani et al. 2000; Demirbas 2004; Celik and Demirbas 2005; Suhas et al. 2007;

Crisafully 2008; Wu et al. 2008). The adsorption of lignin films prepared on various substrates from different lignins and lignin model compounds by various methods have also been reported (Nenkova 2007; Norgren et al. 2006, 2007; Pasquini et al. 2002; Vainio et al. 2004). Most recently, Notley and Norgren (2010) have investigated the surface energy and wettability of spin-coated thin films of kraft lignin. Their studies show that the surface energy of the lignin film is similar to that of cellulose; but the contact angle of water on lignin is much higher than that on cellulose. The lignin surface contains charged functional groups that may attract charged oil droplets.

To the best of our knowledge, there has been no report that describes the utilization of kraft lignin for human use in the control of obesity. The objectives of this study are to explore kraft lignin as a promising alternative to chitosan and to highlight its advantages in comparison to chitosan for adsorption of dietary oils. In the present work, the adsorption isotherm and kinetics for six different dietary oils onto kraft lignin were investigated. Our study shows that kraft lignin may aid in solving the obesity problem, which leads to many serious health complications, based on its dual action as an indigestible natural product and an economical adsorbent.

## EXPERIMENTAL

### Chemicals and Materials

All chemicals used were commercially available analytical grades. Potassium hydroxide (Canadawide Scientific Ltd.), sulfuric acid (Sigma 99.999% purity), hydrochloric acid (Anachemia, Canada), hydrogen phosphate dibasic (Sigma-Aldrich), potassium chloride (Anachemia), ethyl alcohol (Sigma), chitosan, low molecular weight (Aldrich) and phenolphthalein indicator (Sigma), cottonseed oil (Sigma C-7767), corn oil (Mazola product of USA), sunflower oil (Unico Inc., product of Canada), extra virgin olive oil (Great Value Walmart Canada - imported from Italy), canola oil (No Name product of Canada), and peanut oil (Great Value Walmart Canada - product of USA) were employed.

Standard stock solution 0.5 $mol.L^{-1}$ alcoholic KOH was prepared by dissolving 28.05 g KOH in 100 mL of distilled water and completing the volume to 1 L with 95% ethyl alcohol. Standard stock solution 0.5 $mol.L^{-1}$ HCl was prepared by transferring 41.5 mL of conc. HCl and completing to 1 L volume with distilled water. Acidic buffer solution (pH = 1.7) was prepared by mixing 195 mL of 0.2 $mol.L^{-1}$ HCl solution with 750 mL of 0.2 $mol.L^{-1}$ KCl solution was used to prepare buffer solution of pH = 1.7. Basic buffer solution of pH = 8 was prepared by mixing 955 mL of 0.1 $mol.L^{-1}$ $Na_2HPO_4$ solution with 45 mL of 0.1 $mol.L^{-1}$ HCl solution was used to obtain a 1 L buffer solution of pH = 8.0. The pH was checked using a pH meter. Lignin samples were prepared by passing carbon dioxide ($CO_2$) gas through black liquor supplied by a local pulp and paper mill. The precipitated lignin was further purified using a dilute sulphuric acid solution (due to the low solubility of lignin in acid media) (Wallmo et al. 2009).

## Determination of Vegetable Oils

In dry glass stoppered conical flasks, 0.2, 0.4, 0.6, 0.8, and 1 g of oil were weighed, respectively. A known excess 25 mL of 0.5 mol.$L^{-1}$ alcoholic KOH were added using a burette. Each flask was fitted to a water condenser and was heated in a steam water bath for 60 minutes for complete saponification of the oil sample with occasional shaking. The flask was cooled and two drops of phenolphthalein were added. The residual amount of alcoholic KOH was titrated against 0.5 mol.$L^{-1}$ HCl until the pink color disappeared. A blank of similar reagents was carried out. The calibration curve was plotted between the weight of oil sample in grams and the millimoles of KOH consumed by the oil for complete saponification.

## Lignin and Chitosan Dissolution Study

The dissolution percent of lignin was tested in both acidic pH (1.7) and basic pH (8.0) by gravimetric analysis. The weight of lignin was measured before and after the agitation process, and the difference in weight was calculated in both acidic and basic pH conditions. A similar procedure was performed for chitosan in a basic medium (pH=8.0).

## Adsorption of Oils on Lignin and Chitosan

In a conical flask, 0.1 g lignin (or chitosan) and 0.6 g oil were weighed; 20 mL of buffer solution (acidic or basic) was added. The temperature was adjusted to 37 $^{o}$C, and a thermostatically controlled water bath with shaking was used for 30 minutes. The solution was centrifuged, and the centrifugate was transferred into a glass stoppered conical flask to which 25 mL of 95 % ethyl alcohol and 25 mL of 0.5 mol.$L^{-1}$ alcoholic KOH were added. The flask was fitted to a water condenser and heated in a steam water bath for 60 minutes with occasional shaking for complete saponification of the oil sample. The flask was cooled, and two drops of phenolphthalein were added. The residual amount of alcoholic KOH was titrated against 0.5 mol.$L^{-1}$ HCl until the pink color disappeared. A blank of similar reagents was carried out. The weight of oil left in solution at equilibrium was calculated by substituting in the calibration equation for each oil. The weight of oil adsorbed on the lignin surface is equal to ($W_o$– $W_e$). The adsorption capacity ($q_e$) of lignin was calculated using Eq. (1),

$$q_e = \frac{W_o - W_e}{M} \quad (1)$$

where $q_e$ is the amount of oil adsorbed at equilibrium per unit weight of lignin determined in g/g, $W_o$ is the initial weight of oil sample (g), $W_e$ is the equilibrium weight of oil sample in solution after the adsorption process (g), and $M$ is the mass of lignin adsorbent (g). The removal percent can be calculated as well, using Eq. (2):

$$R\% = \frac{W_o - W_e}{M} \text{ X } 100 \quad (2)$$

## Effect of Agitation Time on the Adsorption of Oils on Lignin Surface

In a conical flask, 0.6 g olive oil, 100 mg lignin, and 20 mL of acidic buffer solution (pH 1.7) were added, and the solution was stirred for different time intervals at

37 $^{o}$C. The solution was centrifuged, and the centrifugate was transferred into a glass-stoppered conical flask into which 25 mL of 95 % ethyl alcohol and 25 mL of 0.5 mol.L$^{-1}$ alcoholic KOH were added. The flask was fitted to a water condenser and heated in a steam water bath for 60 minutes with occasional shaking for complete saponification of the oil sample. The flask was cooled, and two drops of phenolphthalein were added. The residual amount of alcoholic KOH was titrated against the 0.5 mol.L$^{-1}$ HCl until the pink color disappeared. A blank of similar reagents was carried out. The weight of oil adsorbed on lignin surface was calculated using the calibration equation.

### Effect of the Amount of Lignin on the Adsorption of Oils

In a conical flask, 0.6 g olive oil was accurately weighed, whereby 20, 40, 60, 80, and 100 mg of lignin were weighed and added, respectively. Then 20 mL of acidic buffer solution (pH 1.7) was added, and the solution was stirred for 30 min at 37 $^{o}$C. The same procedure described in section 2.5 was used to determine the amount of the oil adsorbed on the lignin samples.

## RESULTS AND DISCUSSION

Volumetric analysis was applied to measure the saponification value for an oil sample. The amount of fatty acids present in the oil sample can be determined quantitatively by applying a simple and sensitive residual titrimetric technique (back titration) for the known excess standard KOH solution used for oil saponification against a standard HCl solution. The linear relationship between the fatty acid content and the oil sample weight enables the calculation of the weight of oil remaining in solution at equilibrium after the adsorption process has been established. The weight of the residual amount of oil is obtained from the calibration curve by converting the KOH volume in milliliters to millimoles using the relationship:

Number of millimoles of KOH = Molarity X Volume in milliliters (3)

The relationship between the weight of the oil sample and the amount of alcoholic KOH standard solution consumed in the saponification process was plotted and was found to be linear for the six different oil samples. The regression equations are shown in Table 1,

**Table 1.** Calibration Equations for Vegetable Oils Using the Titrimetric Method

| Sample | Regression Equation | $R^2$ | Equation number |
|---|---|---|---|
| canola oil | $Y = 3.806\,X - 0.016320$ | 0.9996 | (3) |
| corn oil | $Y = 4.001\,X - 0.139300$ | 0.9999 | (4) |
| cottonseed oil | $Y = 4.030\,X - 0.122200$ | 0.9999 | (5) |
| olive oil | $Y = 3.794\,X + 0.090430$ | 0.9993 | (6) |
| sunflower oil | $Y = 3.882\,X - 0.002511$ | 0.9997 | (7) |
| peanut oil | $Y = 3.728\,X + 0.003446$ | 0.9994 | (8) |

where *Y* is the number of millimoles of standard KOH solution consumed in saponification of the oil sample, and X is the weight of the oil sample in grams.

## Effect of pH on the Dissolution of Lignin and Chitosan

The dissolution percent of lignin was tested at pH (1.7) and pH (8.0) by gravimetric analysis. The value pH 1.7 is the median for the stomach pH range (1 to 3.5). The digestion of edible oils begins in the small intestine lumen at pH 6 to 8 (Marks et al. 1996). The ileum is the main site of absorption for dietary oil and fat. The pH 8.0 was studied to ensure that the oil adsorption that occurred in the stomach acid pH equivalent is irreversible, and is not affected by the transition to the alkaline pH of the intestine. The weight of lignin was measured before and after the agitation process under both the acidic and basic pH conditions. Lignin showed high stability in both media and resisted dissolution. The dissolution percent was calculated and was found to be 15% in the acidic medium (pH=1.7) and 18% in the basic medium (pH=8.0). Conversely, chitosan was found to be completely soluble in the acidic medium, as it contains basic amino groups in its structure. It formed a single phase viscous emulsion solution with the adsorbed oil. Therefore, it could not be isolated and tested for its adsorption efficiency under acidic conditions. However, a gravimetric analysis was performed for chitosan under the basic pH and the results were compared to those of lignin. The dissolution level of chitosan in the basic medium (pH=8.0) was found to be 12 %.

## Adsorption of Oils on Lignin and Chitosan Surfaces

The linear relationship between the weight of the oil sample and the amount of alcoholic KOH standard solution consumed in the saponification process was used to calculate the concentration of oil remaining in solution after the adsorption process was established on the surfaces of the lignin or chitosan adsorbents. The adsorption efficiency of lignin and chitosan, when challenged with six different types of vegetable oils, was tested and compared. As shown in Table 2, lignin exhibited excellent adsorption efficiencies for the selected oils in both acidic and basic pHs. The removal proportion for each of canola oil, olive oil, sunflower oil, corn oil, cottonseed oil, and peanut oil ranged from (90.03 to 97.38%) when lignin was used as the adsorbent. These results are comparable to the chitosan adsorbent. The adsorption capacity ($q_e$) of lignin for these oils was calculated using Eq. (1).

**Table 2.** Oil removal percentages by lignin and chitosan under the acidic (pH =1.7) and base (pH = 8.0) conditions

| Oil Sample | Lignin | | Chitosan |
|---|---|---|---|
| | pH = 1.7 | pH = 8.0 | pH = 8.0 |
| Canola oil | 96.94 % | 93.00 % | 94.90 % |
| Olive oil | 97.38 % | 94.48 % | 99.58 % |
| Sunflower oil | 95.60 % | 95.43 % | 100.00 % |
| Corn oil | 90.03 % | 91.07 % | 93.15 % |
| Cottonseed oil | 90.80% | 90.80 % | 100 .00 % |
| Peanut oil | 95.68 % | 93.45 % | 94.57 % |

As shown in Table 3, the adsorption capacity ($q_e$) of lignin for the removal of different dietary oils is very high under either the acidic (pH=1.7) or basic (pH = 8.0) conditions; results were in the range of 5.3 to 6.0. These results are comparable to those of chitosan under the basic (pH = 8.0) condition.

**Table 3.** Adsorption Capacity ($q_e$) of Lignin and Chitosan in Acidic (pH=1.7) and Basic (pH = 8.0) Media for the Removal of Different Dietary Oils using 0.1 g Lignin, 0.1 g Chitosan, and 0.6 g Oil

| Oil Sample | Lignin | | Chitosan |
|---|---|---|---|
| | pH = 1.7 | pH = 8.0 | pH = 8.0 |
| Canola oil | 5.70 | 5.30 | 5.69 |
| Olive oil | 5.84 | 5.94 | 5.98 |
| Sunflower oil | 5.74 | 5.54 | 6.00 |
| Corn oil | 5.40 | 5.46 | 5.59 |
| Cottonseed oil | 5.45 | 5.45 | 6.00 |
| Peanut oil | 5.74 | 5.61 | 5.67 |

## Surface Characterization of Lignin by Scanning Electron Microscopy (SEM)

SEM was used to characterize the morphology and surface structure of vegetable oils when adsorbed to lignin. The lignin surface morphology subsequent to oil adsorption was compared to lignin surface images taken prior to the oil adsorption, as shown in Fig. 1. Lignin exhibits a polygonal shape with multiple conchoidal fracture surfaces (Sharma et al. 2004). It has clear and bumpy layers that are arranged homogenously. A dramatic modification of the surface structure and surface appearance of lignin was obtained after oil adsorption. As seen from the SEM image (Fig. 1B), the lignin surface was covered with mud-like pores due to the oil molecule adsorption. The surface morphology softened and exhibited wide and deep melted features which were surrounded by "islands".

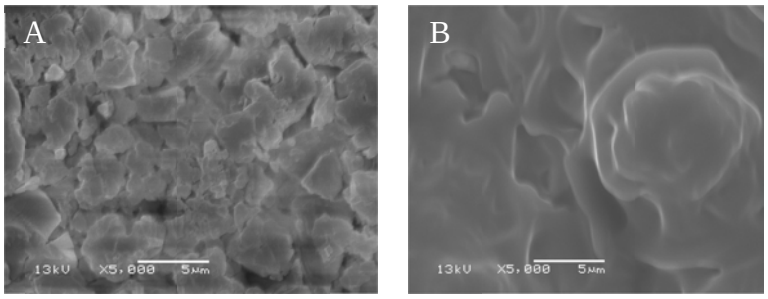


**Fig. 1.** Scanning electron microscopic images of (A) lignin before oil adsorption, (B) after canola oil adsorption.

## Effect of Agitation Time and the Amount of Lignin on the Oil Adsorption

Olive oil was selected to undergo the optimization experiments. The effect of the agitation time on the adsorption levels of olive oil on the lignin surface was studied in

acidic medium at different time intervals, as shown in Fig. 2. The equilibrium state was established at 30 minutes of agitation.

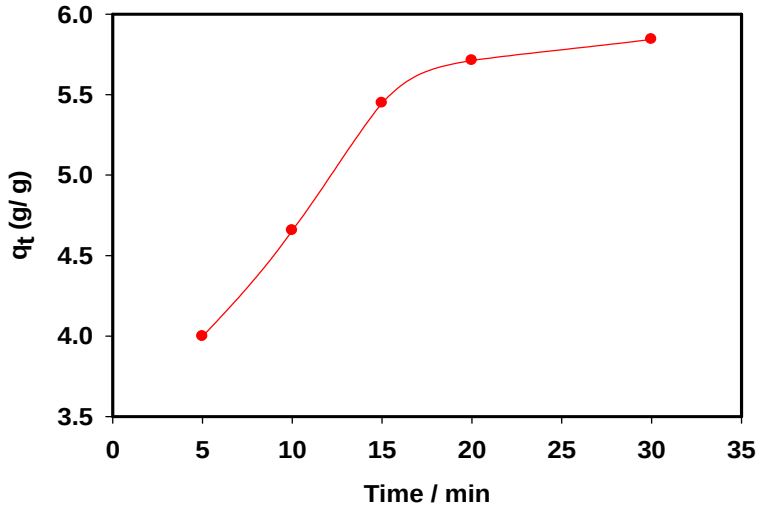


**Fig. 2.** Effect of agitation time on the adsorption of olive oil at pH 1.7 on the lignin surface using 0.1 g lignin, 0.1 g chitosan, and 0.6 g oil

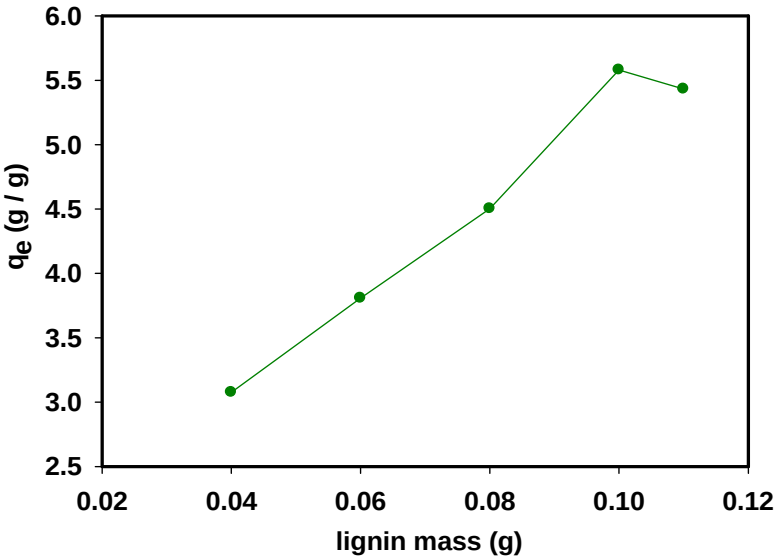


**Fig. 3.** Effect of the lignin powder concentration on the adsorption of oil at pH 1.7 using 0.6 g oil

Figure 3 displays the relationship between the amount of oil adsorbed on the lignin surface and the amount of lignin powder distributed in the solution. Experimental results clearly illustrate that at lower initial oil concentrations, only a small amount of lignin is required. As seen in Figure 3, the amount of oil adsorbed per unit mass of lignin increased linearly with the level of the amount of lignin. At high oil concentrations, the

available adsorption sites become diminished, suggesting that the adsorption process is highly dependent on the initial oil concentration.

## Adsorption Isotherm

The adsorbability of lignin for vegetable oils can be quantified by using an adsorption isotherm model. The ones most commonly used are the Langmuir and Freundlich isotherm models (Demirbas 2004; Celik and Demirbas 2005; Ibrahim et al. 2009; Guo et al. 2008; Najim et al. 2009). These models are widely used for explaining experimental adsorption data. The Langmuir isotherm is considered in cases of the physisorption of gases or liquids on solids when only a monolayer of adsorbate is formed. This is considered to be a prime limitation of the Langmuir isotherm model, since it is well known that during the physisorption process, multiple layers of adsorbate can be formed. The Freundlich isotherm is typically used as an empirical adsorption model for solid-liquid systems. Freundlich described the adsorption of a single adsorbate in an aqueous solution as a reversible equilibrium that is established in a few minutes at a fixed temperature (Freundlich 1924). At low solute concentrations, the amount of adsorbed adsorbate increases with an elevation in solution concentration. The Freundlich model was used to describe oil adsorption (Proctor and Toro-Vazquez 1996). The Freundlich isotherm model is represented by Eq. 9,

$$\log q_e = \log K_f + 1/n \log C_e \quad (9)$$

where $q_e$ is the amount of vegetable oil adsorbed per gram of adsorbent (mg/g), $C_e$ is the equilibrium concentration of vegetable oil in solution (mg/mL), and $K_f$ and $n$ are constants incorporating all the factors affecting the adsorption capacity and adsorption intensity respectively. The $K_f$ and $n$ values can be obtained from the linear plot of log $q_e$ versus log $C_e$, whereby the steeper the slope, the greater the adsorption efficiency of the adsorbent.

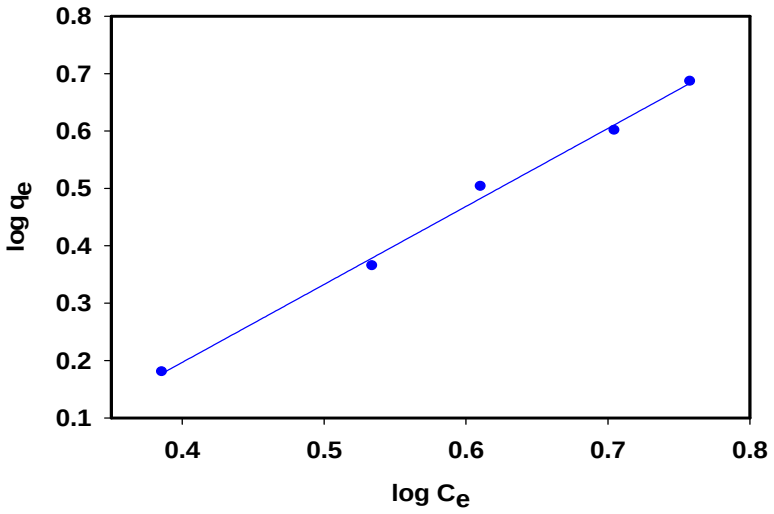


**Fig. 4.** Freundlich isotherm constants for the adsorption of the olive oil on lignin surface using 0.1 g lignin and (0.2 – 0.6) g oil

The adsorption parameters are the slope $1/n$ = 1.358 and the intercept log $K_f$ = - 0.3466 where $K_f$ is an empirical constant related to the capacity of the adsorbent to the adsorbate and n is a constant related to the affinity of the adsorbate toward the surface.

## Adsorption Kinetics

The pseudo-first order and the pseudo-second order kinetic models have been used to study the adsorption process (Ibrahim et al. 2009; Guo et al. 2008; Najim et al. 2009). The applicability of these two kinetic models was investigated in this study to examine the adsorption of vegetable oils on the surfaces of lignin. The best fit model was determined based on the linear regression correlation coefficient. The Langergren Eq. (10) for the pseudo-first order kinetic describes the adsorption process as follows,

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}\ t \qquad (10)$$

where $q_e$ and $q_t$ are the amount of the vegetable oil adsorbed at time $t$ and at equilibrium time respectively in mg/g, $k_1$ is the pseudo-first order rate constant in $min^{-1}$. According to the adsorption equation, the experimental results can be plotted to get the relation between log ($q_e - q_t$) versus $t$. The data showed that the adsorption of vegetable oil on the surfaces of lignin does not fit well with pseudo-first order process (Fig. 5A).

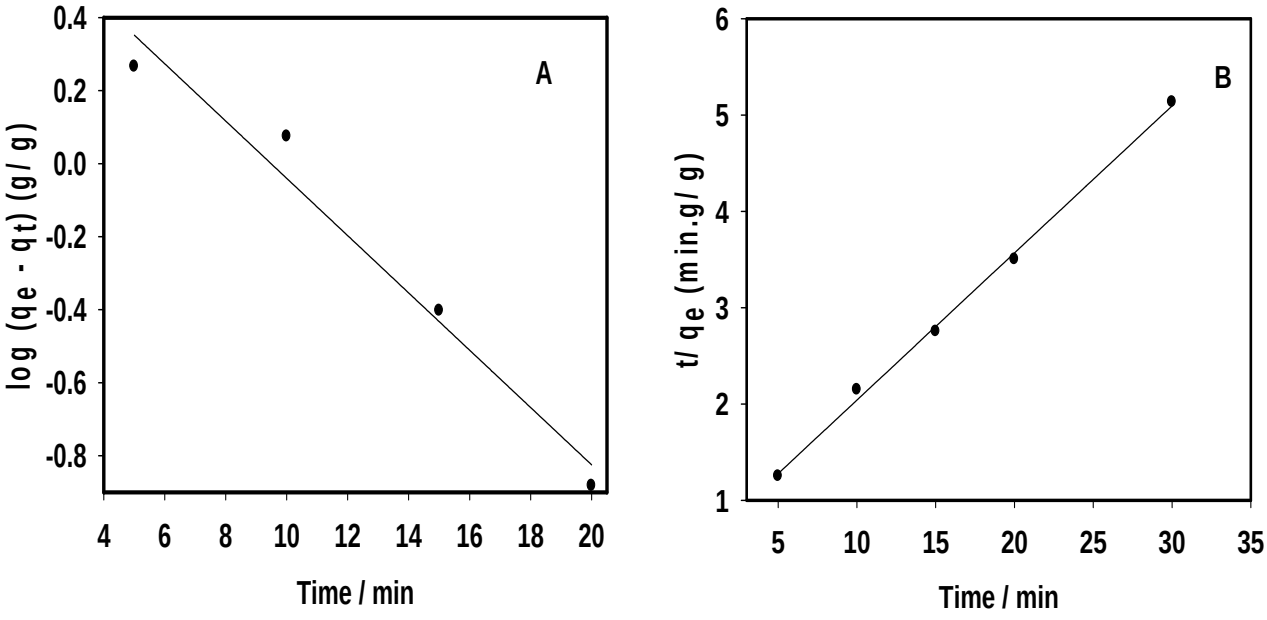


**Fig. 5.** (A) Plot of pseudo-first order kinetic model (B) pseudo-second order kinetic model for the adsorption of olive oil on lignin at pH 1.7.

The pseudo- second order kinetic model is expressed in Eq. (11) as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}} + \frac{t}{q_e} \quad (11)$$

where $k_2$ is the rate constant of the pseudo-second order adsorption (g/mg.min), and the plot of $tq_t^{-1}$ versus t shows a linear relationship with a coefficient of determination $R^2$ = 0.9976. The adsorption capacity ($q_e$) and $k_2$ values were calculated as 6.55 and 0.045 from the slope and the intercept of the plot in Fig. 5B, respectively. The calculated value of the adsorption capacity $q_{e\,(cal)}$ for the pseudo-second order model was found to be 6.55, and it agreed well with the experimental one $q_{e(exp).}$ The pseudo-second order kinetic model was found to be applicable. The linear plot in Fig. 5B showed good agreement with the pseudo-second order kinetic model.

## CONCLUSIONS

The adsorption efficiency of lignin was investigated with six dietary plant oils at biological temperature, revealing an adsorption capacity of up to 6 times its own weight. Lignin demonstrates a remarkable stability in both acidic (pH 1.7) and basic (pH 8.0) media. The adsorption of dietary oils on lignin fits the Freundlich model and follows pseudo-second order kinetics. Lignin can maintain its solid state integrity under acidic stomach conditions and it is completely insoluble, while chitosan forms a single phase viscous emulsion with oil under the same conditions. Our study showed that lignin may serve as an important component in the battle against obesity and hypercholesterolemia. In such applications lignin may serve as a natural adsorbent, having some advantages relative to chitosan, which is used currently.

## ACKNOWLEDGEMENTS

This work was supported by a Strategic Grant from the Natural Sciences and Engineering Research Council of Canada (NSERC). A. Chen Acknowledges NSERC and the Canada Foundation of Innovation (CFI) for the Canada Research Chair Award in Material and Environmental Chemistry.

## REFERENCES CITED

Ahmad, A. L., Sumathi, S., and Hameed, B. H. (2005). "Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: Equilibrium and kinetic studies," *Water Res.* 39, 2483-2494.

Aman, P., Pettersson, D., Zhang, J., Tidehac, P., and Hallmans, G. (1995). "Starch and dietary fiber components are excreted and degraded to variable extents in ileostomy subjects consuming mixed diets with wheat or oat-bran bread," *J. Nutr*. 125(9),

2341-2347.

Ayorinde, F. O., Garvin, K., and Saeed, K. (2000). "Determination of the fatty acid composition of saponified vegetable oils using matrix-assisted laser desorption/ ionization time-of-flight mass spectrometry," *Rapid Commun. Mass Spectrom*. 14(7), 608-615.

Bokura, H., and Kobayashi, S. (2003). "Chitosan decreases total cholesterol in women: A randomized, double- blind, placebo- controlled trial," *Europ. J. Clin. Nutr*. 57, 721-725.

Bunzel, M., Ralph, J., Marita, J. M., Hatfield, R. D., and Steinhart, H. (2001). "Diferulates as structural components in soluble and insoluble cereal dietary fiber," *J. Sci. of Food and Agr.* 81, 653-660.

Celik, A., and Demirbas, A. (2005). "Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes," *Energ. Source*. 27, 1167-1177.

Chen, S. H., Chen, K. C. and Lien, H. M. (1999). "Determination of fatty acids in vegetable oil by reversed-phase liquid chromatography with fluorescence detection," *J. Chromatogr. A.* 849, 357-369.

Crampton, E. W., and Maynard, L. A. (1938). "The relation of cellulose and lignin content to the nutritive value of animal feeds," *J. Nutr.* 15(4), 383-395.

Crisafully, R., Milhome, M. A. l., Cavalcante, R. M., Silveira, E. R., Keukeleire, D. D., and Nascimento, R. F. (2008). "Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin," *Biores. Technol.* 99, 4515-4519.

Demirbas, A. (2004). "Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignification," *J. Hazard. Mater. B.* 109, 221-226.

Dizhbite, T., Zakis, G., Kizima, A., Lazareva, E., Rossinskaya, G., Jurkjane, V., Telysheva, G., and Viesturs, U. (1999). "Lignin - A useful bioresource for the production of sorption-active materials," *Biores. Technol.* 67, 221-228.

Ellis, G. H., Matrone, G., and Maynard, L. A. (1964). "A 72 % sulfuric acid method for the determination of lignin and its use in animal studies," *J. Anim. Sci.* 5, 285-289.

Fahey, G. C., Jr., and Jung, H. G. (1983). "Lignin as a marker in digestion studies: A review," *J. Anim Sci*. 57, 220-225.

Forbes, E. B., Elliot, R. F., Swift, R. W., James, W. H., and Smith, V. F. (1964). "Variation in determination of digestive capacity of sheep," *J. Anim. Sci*. 5, 298-307.

Freundlich, H. (1924). *The Elements of Colloidal Chemistry*, translated by George Barger, Dutton and Company publisher, NY, pp. 58- 61.

Gray, F. V. (1975). "The digestion of cellulose by sheep. The extent of cellulose digestion at successive levels of the alimentary tract," *J. Exp. Biol*. 24, 15-21.

Guerciolini, R., Radu-Radulescu, L., Boldrin, M., Dallas, J., and Moore, R. (2001). "Comparative evaluation of fecal fat excretion induced by Orlistat and chitosan," *Obes. Res*. 9(6), 364-367.

Gunstone, F. D. (2002). *Vegetable Oils in Food Technology: Composition, Properties and Uses*, Blackwell publishing Ltd, UK, pp. 1-326.

Guo, X., Zhang, S., and Shan, X. Q. (2008). "Adsorption of metal ions on lignin," *J. Hazard. Mater.* 151, 134-142.

Heitner, C., Dimmel, D., and Schmidt, J. (2010). *Lignin and Lignans*, Taylor and Francis group, USA., pp. 1-50.

Ibrahim, M. N., Ngah, W. S., Norliyana, M. S., and Daud, W. R. (2009). "Copper (II) biosorption on soda lignin from oil palm empty fruit bunches (EFB)," *Clean*. 37(1), 80-85.

Knudsen, K. E. B. (1997). "Carbohydrates and lignin contents in plant materials used in animal feeding," *Anim. Feed Sci. Tech.* 67, 319-338.

Lalvani, S. B., Hubner, A., and Wiltowski, T. S. (2000). "Chromium adsorption by lignin," *Energ. Sourse.* 22, 45-56.

Lowry, R. R., and Tinsley, I. J. (1976). "Rapid colorimetric determination of free fatty acids," *JAOCS.* 53(7), 470-472.

MacDonald, I. R. C., and Campbell, W. G. (1952). "Acid – soluble lignin," *Nature*. 169, 33-40.

Marks, D. B., Marks, A. D., and Smith, C. M. (1996). "Lipid metabolism," In: *Basic Medical Biochemistry*, Velker, J. (ed.), Lippincott Williams & Wilkins, USA.

Najim, T., Elais, N. J., and Dawood, A. A. (2009). "Adsorption of copper and iron using low cost material as adsorbent," *E-J. of Chem.* 6(1), 161-168.

Nenkova, S. (2007). "Study of sorption properties of lignin-derivatized fibrous composites for the determination of oil polluted receiving waters," *Biores.* 2(3), 408-418.

Norgren, M., Notley, S. M., Majtnerova, A., and Gellerstedt, G. (2006). "Smooth model surfaces from lignin derivatives. I. Preparation and characterization," *Langmuir* 22, 1209-1214.

Norgren, M., Gardlund, L., Notley, S. M., Htun, M., and Wagberg, L. (2007). "Smooth model surfaces from lignin derivatives. II. Adsorption of polyelectrolytes and PECs monitored by QCM-D," *Langmuir* 23, 3737-3743.

Notley, S. M., and Norgren, M. (2010). "Surface energy and wettability of spin-coated thin films of lignin isolated from wood," *Langmuir* 26(8), 5484-5490.

Pasquini, D., Balogh, D. T., Antunes, P. A., Constantino, J. L., Curvelo, A. A. S., Aroca, R. F., and Oliveira, O. N. (2002). "Surface morphology and molecular organization of lignins in Langmuir-Blodgett films," *Langmuir* 18, 6593-6596.

Peternele, W. S., Hechenleitner, A. A. W., and Pineda, E. A. G. (1999). "Adsorption of Cd (II) and Pb (II) onto fractionized formic lignin from sugar cane bagasse," *Biores. Technol*. 68, 95-100.

Porter, A., and Singleton, A. G. (1971). "The degradation of lignin and quantitative aspects of ruminant digestion," *Brit. J. Nutr.* 25, 3-10.

Proctor, A., and Toro-Vazquez, J. F. (1996). "The Freundlich isotherm in studying adsorption in oil processing," *JAOCS.* 73(12), 1627-1633.

Tolba, R., Tian, M., Wen, J., Jiang, Z.-H., and Chen, A. (2010). "Electrochemical oxidation of lignin at $IrO_2$-based oxide electrodes," *J. Electroanal. Chem.* 649, 9-15.

Sharma, R. K., Wooten, J. B., Baliga, V. L., Lin, X, Chan, W. G. and Hajaligol, M. R. (2004). "Characterization of chars from pyrolysis of lignin," *Fuel* 83, 1469-1482.

Suhas, Carrott, P. J. M., and Carrott, M. M. R. (2007). "Lignin – from natural adsorbent to activated carbon: A review," *Biores. Tech.* 98, 2301-2312.

Tian, M., Wen, J., MacDonald, D., Asmussen, R. M., and Chen, A. (2010). "A novel approach for lignin modification and degradation," *Electrochem. Commun.* 12, 527-530.

Vainio, U., Maximova, N., Hortling, B., Laine, J., Stenius, P., Simola, L. K., Gravitis, J., and Serimaa, R. (2004). "Morphology of dry lignins and size and shape of dissolved kraft lignin particles by X-ray scattering," *Langmuir* 20, 9736-9744.

Van Soest, P. J. (1982). "Refractory and Inhibitory substances," In: *Nutritional Ecology of the Ruminants*, O. and B. Books, Inc., Corvallis, OR, pp. 118.

Wallmo, H., Richards, T., and Theliander, H. (2009). "An investigation of process parameters during lignin precipitation from kraft black liquors: A step towards an optimised precipitation operation," *Nord. Pulp Paper Res. J*. 24(2), 158-164.

Woodman, H. E., and Stewart, J. (1932). "The mechanism of cellulose digestion in the ruminant organism. The action of cellulose splitting bacteria on the fiber of certain typical feeding stuffs," *J. Agric. Sci*. 22, 527-547.

Wu, Y., Zhang, S., Guo, X., and Huang, H. (2008). "Adsorption of chromium (III) on lignin," *Biores. Technol.* 99, 7709-7715.

Article submitted: January 19, 2011; Peer review completed: February 21, 2011; Revised version received and accepted: March 3, 2011; Published: March 6, 2011.