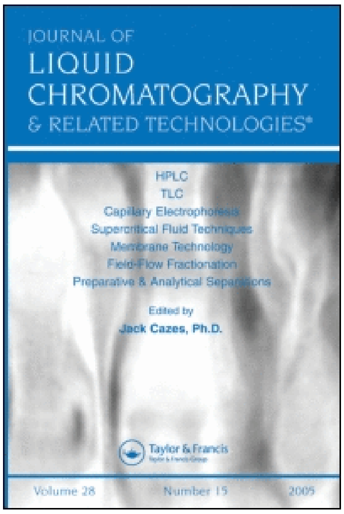

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

PHOSPHATE ADSORPTION ON CHITOSAN-Fe^{III}-CROSSLINKING: BATCH AND COLUMN STUDIES

Tathyane Fagundes[a]; Estefânia Luiza Bernardi[a]; Clóvis Antonio Rodrigues[a]
[a] Universidade do Vale do Itajaí (UNIVALI), Itajai, SC, U.S.A.

To cite this Article Fagundes, Tathyane , Bernardi, Estefânia Luiza and Rodrigues, Clóvis Antonio(2001) 'PHOSPHATE ADSORPTION ON CHITOSAN-Fe^{III}-CROSSLINKING: BATCH AND COLUMN STUDIES', Journal of Liquid Chromatography & Related Technologies, 24: 8, 1189 — 1198

To link to this Article: DOI: 10.1081/JLC-100103441

URL: http://dx.doi.org/10.1081/JLC-100103441

J. LIQ. CHROM. & REL. TECHNOL., 24(8), 1189–1198 (2001)

PHOSPHATE ADSORPTION ON CHITOSAN-Fe^{III}-CROSSLINKING: BATCH AND COLUMN STUDIES

Tathyane Fagundes, Estefânia Luiza Bernardi, and Clóvis Antonio Rodrigues*

NIQFAR- Núcleo de Investigações Químico-Farmacêuticas
CCS, Universidade do Vale do Itajaí (UNIVALI), CEP 88,
302-202, Itajai, SC., Brazil

ABSTRACT

Eutrophication is the over fertilization of a body of the water by nutrients resulting in enhanced algae growth, and phosphate is usually identified as the cause. In this work, the adsorption of phosphate on chitosan-iron(III)-crosslinked (CH-Fe^{III}-CL) was investigated in an experiment of solid-phase extraction. The isotherm adsorption, kinetic adsorption, and pH study were carried out in thermostatically-controlled batches. The dynamic studies were drivers in glass columns. Batch study shows that phosphate adsorption becomes constant after 60 min, 7.0 is optimal pH for phosphate adsorption. Affinity constant and maximum adsorption capacity determined by Langmuir equation were 44.4 L min^{-1} and 131 mg g^{-1}. As expected, an increase in the flowrate reduced the breakthrough volume (180 and 230 mL), exhaustion volume (380 and 420 mL), breakthrough sorption capacity (18 and 23 mg g^{-1}), and exhaustion sorption capacity (32.4 and

---

*Corresponding author.

61.4 mg g^{-1}) for 2.5 mL min^{-1} and 1.0 mL min^{-1}. Such a decrease can be ascribed to a lower residence time.

INTRODUCTION

Considerable attention is now being paid to solid-phase extraction (SPE) as a way to isolate, separate, and concentrate components from a sample. In SPE, the extractant is a porous, particulate solid, which has a large surface area available for interaction with the liquid sample solution.[1]

Phosphate occurs naturally in a variety of chemical forms, and is widely distributed in soils, rocks, and oceans. The ecological importance of the phosphate is due to its role in the metabolism of living organisms. Phosphates are a major factor in the environmental problem of eutrophication.[2] Eutrophication is the process of nutrient enrichment that stimulates algae blooms, primary productivity, and massive growth of macrophytes.[3-5]

Although eutrophication has been recognized as a significant problem in both freshwater and marine environment for more than three decades, this problem has not been solved thus far.[5]

The volume of wastewater generated by human population is typically large, and removal of nutrients from such large amounts of wastewater is expensive. The cost of secondary treatment (which only removes some 30-40% of N and P) for example, is some 3-4 times more expensive than that of primary treatment.[4,5]

Recent developments in environmental quality standards highlight the need for improved wastewater treatment. Biosorption is recognized as an alternative technique to remove pollutants.[6]

Chitosan is a nontoxic natural polysaccharide with high molecular mass, which consists of glucosamine in a 1-4 linkage. Because of its presence in many free amine groups, this polymer can form a polymer-metal complex with many metals, such as Cd^{2+}, Cu^{2+}, Pb^{2+}, Fe^{2+}, MoO_4^{2-} and is, thus, used as a metal-ion sorbent in wastewater.[6-8]

Removal of phosphate from aqueous solution has been studied using iron(III) doped alginate gel and iron(II) chitosan complex.[9,10]

This paper reports the application of iron(III) chitosan-crosslinking (CH-Fe^{III}-CL) to remove phosphate from aqueous solution in batch and column experiments.

EXPERIMENTAL

Preparation of CH-Fe^{III}-CL

The chitosan was dissolved in a $Fe(NO_3)_3$ 0.1 M aqueous solution for 4 hours. An orange precipitate was obtained after addition of acetone. The solid was filtered and washed with acetone for remove excess of $Fe(NO_3)_3$, and finally dried in vacuum. After that, the solid was put in contact with glutaraldehyde 15% (in acetone) solution for 2 hours. Chemical cross-linking of chitosan with glutaraldehyde occurs by a Shiff's reaction on aldehyde groups on glutaraldehyde with amine group. The polymer was characterized following the procedure described in literature.[11]

The solid was size fractionated using U.S. standard sieves and stored in a desiccator. The 100 x 150 mesh sizes were utilized in experiments reported in the present study.

Batch Experiments

Sorption isotherm studies were conducted in test tubes gently shaken at 25.0 ± 0.5°C. The pH solution was adjusted with either nitric acid or sodium hydroxide, and the pH was measured with an Orion 720A pH meter.

The phosphate stock solution, 570 mgL^{-1}, for spectrophotometric analyses was prepared from KH_2PO_4 that had been dried in an oven at 105°C for 1 hour and dissolved in Milli Q water.

Ten mg of CH-Fe^{III}-CL (85mg g^{-1} of iron) was contacted with 10 mL of phosphate solution, initial concentration (1-10 mgL-1). After the specified reaction time, the sorbent was removed from solution by filtration. By comparison, initial and final concentration of phosphate in solution, and capacities could be calculated. The phosphate concentration of the solution was measured using the molybdenum blue spectrophotometric method.[12] The analyses were carried out in the spectrophotometer UV/Vis Shimadzu UV 1601.

The adsorption isotherm was plotted according to the adsorption capacity vs. the final concentration phosphate in the solution.

Sorption Kinetic

Kinetic studies were performed by mixing CH-Fe^{III}-CL, (50 mg) with 10 mL of the KH_2PO_4 (100 mg L^{-1}) solution with agitation at 25 ± 0.5°C. After the specified reaction time, the solid was removed by filtration and solutions were analyzed, as described previously.

Column Experiments

Glass column (15 x 0.5 cm) were gravity packed with a sample of 0.5 g of vacuum dried sorbent. The sorbent was placed in the column, in a suspension with water, and allowed to settle.

The flow-rate of the sample solution from the column was controlled by air pressure applied to the top of the column. Samples of the KH_2PO_4 (100 mg L^{-1}) were prepared by dilution of the stock solution in Milli-Q water.

After column preparation, phosphate solutions were percolated through the column until the phosphate concentration in the effluent was equal to the influent. Effluent samples (5 mL) were periodically collected for analysis. The phosphate concentration was measured with the aforementioned methods. After washing the sorbent with distilled water, the phosphate adsorbed was removed with HCl 0.1 M, 0.5 M and NaCl 2.0 M solutions, at a flow-rate (2.0 mL min^{-1}). The elution process was monitored as describe above.

RESULTS AND DISCUSSION

Batch Studies

Kinetic Isotherm

The increase in phosphate adsorption by CH-Fe^{III}-CL with time is shown in Figure 1. The phosphate adsorption becomes constant after 60 min. This kinetic

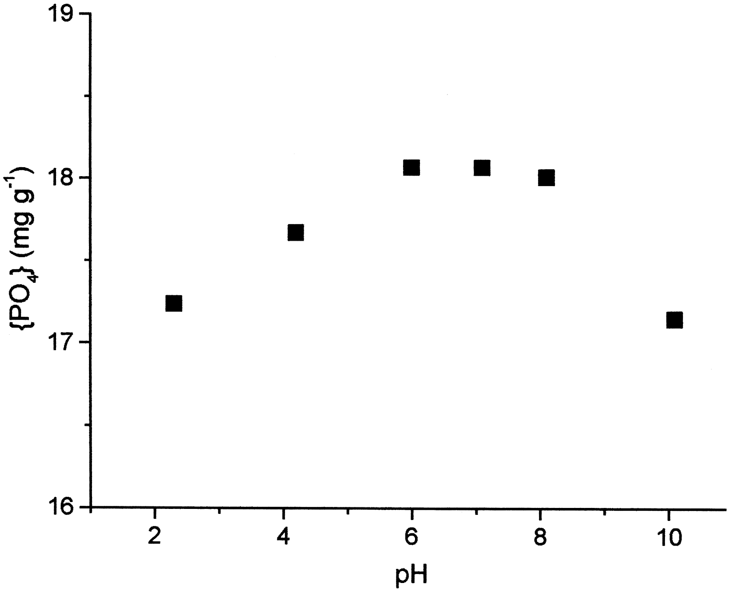

Figure 1. Phosphate adsorption capacity with pH variation. Initial phosphate concentration 100 mgL^{-1}, agitation time 60 min, 50 mg of CH-Fe^{III}-CL. Temperature 25 ± o.5°C.

behavior is different to that observed previously with iron(II)-chitosan complex[10] (3 hours) and iron(III) alginate beads (120 hours).[9]

pH Adsorption

Adsorption of phosphate onto CH-Fe^{III}-CL depends on pH. Maximum adsorption efficiency was observed at pH 7.0, as shown in Figure 2. At this pH, HPO_4^{2-} is the predominant species and the complex $[FeHPO_4]^+$ formation occurs in the polymer surface. The complex formed has a stability constant of 8.36 (solution study).[13] At a lower pH, the neutral species H_3PO_4 is formed predominantly and it results in a decrease of sorption efficiency. At a higher pH, the PO_4^{3-} is the predominant species and also contributes to the reduction of the ability of CH-Fe^{III}-CL to adsorb phosphate.

Adsorption Isotherm

The Langmuir model is commonly used to fit experimental data when solute uptake occurs by a monolayer sorption. The Langmuir model assumes the

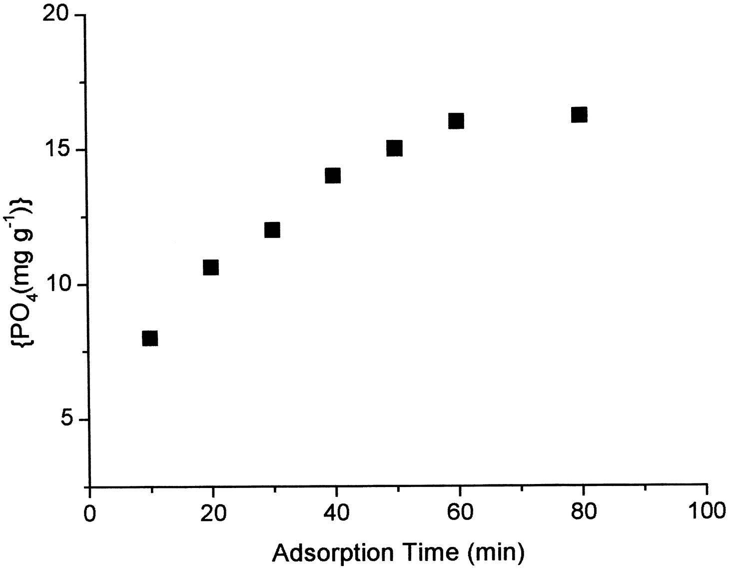

Figure 2. Phosphate adsorption rate of CH-Fe^{III}-CL. Initial phosphate concentration 100 mgL^{-1}, 50 mg of CH-Fe^{III}-CL. Temperature 25 ± 0.5°C.

surface of the sorbent to be homogeneous and the sorption energies to be equivalent for each sorption site.[14] The relationship between the CH-Fe^{III}-CL amount and phosphate concentration in solution, obtained by Langmuir model isotherm adsorption, is shown in Figure 3. The shape of the isotherm showed a rapid initial increase in the adsorption capacity resulting from a high apparent affinity of the CH-Fe^{III}-CL by phosphate ions. Affinity constant and maximum adsorption capacity were determined by Langmuir equation (1):

$$\{PO_4\}\text{sorb} = \frac{K[PO_4]\text{diss}\{CH - Fe^{III} - CL\}}{1 + K[PO_4]\text{diss}}$$

Where

$[PO_4]_{diss}$ = dissolved concentration of phosphate, mg L^{-1};
$\{PO_4\}_{sorb}$ = sorbed concentration, mg phosphate g^{-1} sorbent;

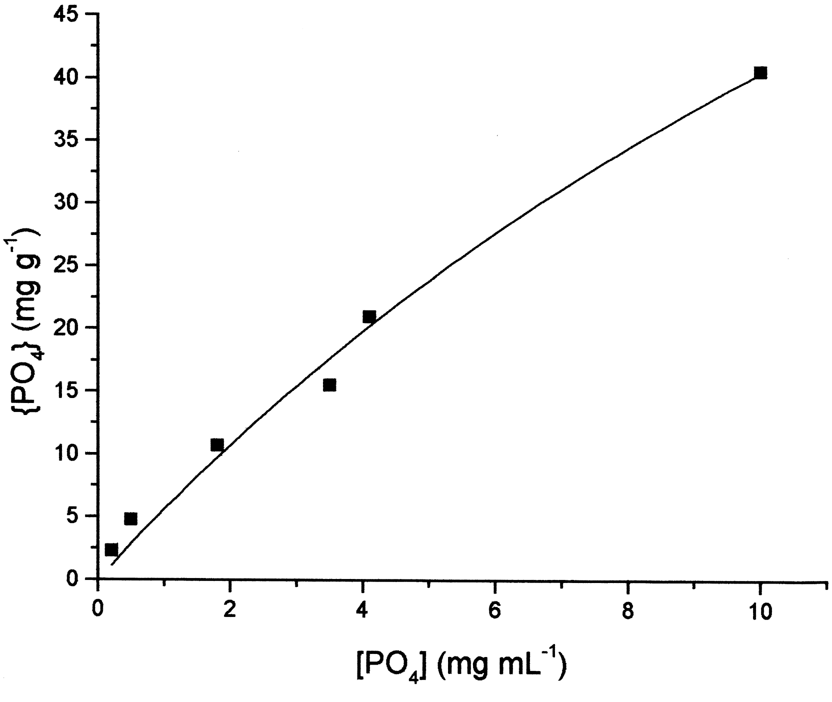

Figure 3. Phosphate adsorption isotherm for CH-Fe^{III}-CL. 50 mg. of CH-Fe^{III}-Cl, agitation time 60 min. Temperature 25 ± 0.5°C.

$\{CH\text{-}Fe^{III}\text{-}CL\}_T$ = saturation (maximum) sorption capacity, mg phosphate/ g sorbent;
K = conditional affinity constant, L mg^{-1}.

Equation 1 was used to fit values of $\{PO_4\}_{sorb}$ and $[PO_4]_{diss}$ from Figure 3, using a nonlinear, least-square regression to obtain the constant K = 44.4 L mg^{-1} and $\{CH\text{-}Fe^{III}\text{-}CL\}_T$ = 131 mg g^{-1} with a correlation coefficient of 0.9936.

Phosphate adsorption capacities of CH-Fe^{III}-CL are much greater than those of iron(II) chitosan complex reported by Jing and Yamaguchi.[10] The stability constant of $[FeHPO_4]$ complex is lower than $[FeHPO_4]^+$, log K 3.60 and 8.36, respectively, (K=[M][L]/[ML]).[13]

Column Study

The breakthrough capacity is defined as the amount of phosphate that can be adsorbed per mass unit of CH-Fe^{III}-CL, before being detected in the outlet of the column. In this work, the breakthrough capacity determined directly from the curve was $(C/C_o).100 = 5$ (Co and C are the phosphate concentrations in the solution at the inlet and outlet of the column, respectively).[15] Breakthrough volume (VB) is reached at 5% of the inlet concentration, while exhaustion volume (VE) is defined as the point corresponding to 95% of the inlet concentration.

In Figure 4, the percentage of phosphate in the effluent outlet is plotted against phosphate solution volume in different flow rates. As expected, an increase in flow rate reduces the breakthrough and exhaustion volume. Table I shows several characteristics of the breakthrough curve obtained with initial phosphate concentration of 100 mg L^{-1} .

As seen in Table 1, breakthrough and exhaustion capacity are lower than the batch capacity value. The contact time of phosphate with adsorbent, in this dynamic study is too short to give sufficient time for phosphate ions to diffuse in the whole mass of the CH-Fe^{III}-CL.

A comparison of the elution efficiencies with 0.1 M HCl, 0.5 M HCl and NaCl 2.0 M as eluents, is shown in Figure 5. Data is expressed as percentages of phosphate eluted calculated in relation to the total phosphate adsorbed (32.4 mg PO_4^{3-} g^{-1} CH-Fe^{III}-CL). As can be seen, a lower concentration of HCl led to lower elution efficiency (10% initial phosphate), but the elution efficiency obtained with 0.5M HCl was 100%; in this case, there occurs the formation of H_3PO_4. On the other hand, higher chloride concentrations (NaCl 0.2 M) do not improve the phosphate elution efficiency (only 40% was eluted in this instance).

In this study, the application of CH-Fe^{III}-CL for phosphate removal was investigated. The results from the sorption experiments demonstrate the possibility of using CH-Fe^{III}-CL to remove phosphate in diluted phosphate solutions, in

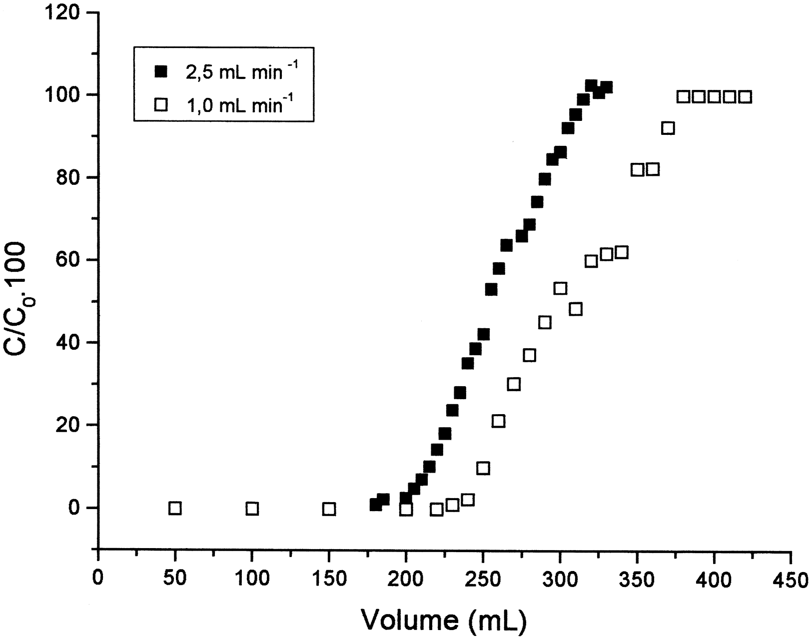

Figure 4. Breakthrough curves for phosphate adsorption at different flow rates. Feed solution phosphate concentration 100 mL/min^{-1}. Column 15 x 0.5 cm), weight of CH-Fe^{III}-CL, 0.5 g.

Table 1. Effect of Flow Rate on Phosphate Adsorption. Initial Phosphate Concentration Solution, 100 mg L^{-1}.

Flow-Rate (mL min^{-1})	V_B [a] (mL)	V_E [b] (mL)	{CH-Fe^{III}-CL}$_B$ [c] (mg g^{-1})	{CH-Fe^{III}-CL}$_E$ [d] (mg g^{-1})
1.0	230	420	23	61.4
2.5	180	380	18	32.4

[a] V_B- breakthrough volume.

[b] V_E- exhaustion volume.

[c] {CH-Fe^{III}-CL}$_B$- breakthrough sorption capacity of phosphate.

[d] {CH-Fe^{III}-CL}$_E$- exhaustion sorption capacity of phosphate.

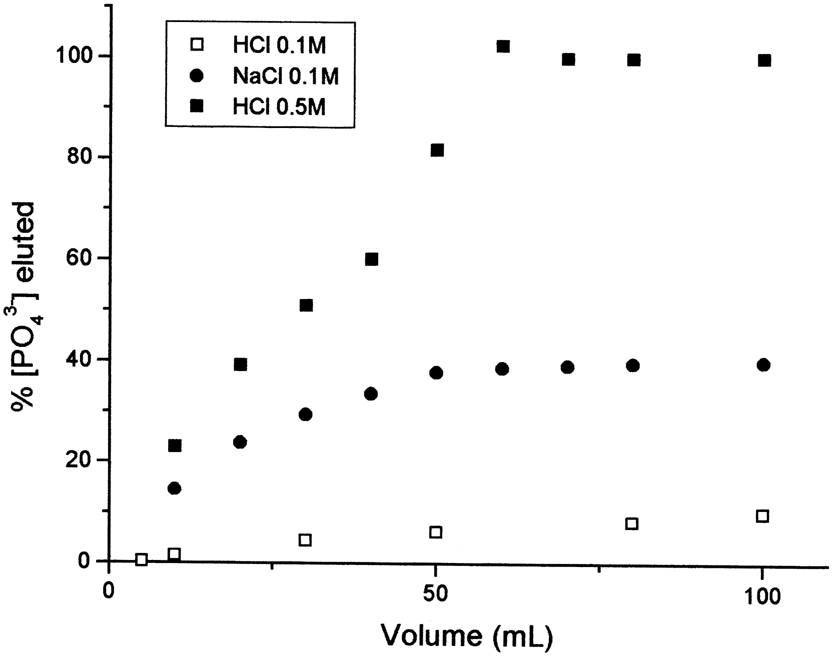

Figure 5. Elution efficiency: percentage of phosphate eluted as a function of eluent volume. Flow rate, 2.5 mL/min^{-1}.

batch or column experiments. Further tests, including the ionic matrix component effects, are needed to evaluate the possibility of applying CH-Fe^{III}-CL to phosphate to remove it from aqueous wastestreams.

ACKNOWLEDGMENT

This work was supported by grants from ProBIC/ProPPEx/UNIVALI.

REFERENCES

1. Fritz, J.S.; Dumont, P.J; Schmidt, L.W. J. Chromatogr. A **1995**, *691*, 133–140.
2. De Marco, R.; Pejcic, B.; Chen, Z. Analyst **1998**, *123*, 1635–1640.
3. Shotyk, W.; Immenhauser-Potthast, I.; Vogel, H.A. J. Chromatogr. A **1995**, *706*, 209–213.

4. Wu, R.S. Mar. Poll. Bull **1999**, *39*, 11–22.
5. Phosphorus & Potassium. Phosphates Removal & Recovery from Wastewater **1998**, *213*, 30–39.
6. Guibal, E.; Milot, C.; Tobin, J.M. Ind. Eng. Chem. Res. **1998**, *37***,** 1454–1463.
7. Argüelles-Monal, W.; Peniche-Covas, C. Angew. Mackomol. Chem. **1993**, *207*, 1–8.
8. Guibal, E.; Milot, C.; Roussy, J. Water, Environ. Res. **1999**, *71*, 10–17.
9. Min, J.H.; Hering , J.G. Water Environ. Res. **1999**, *71*, 169–175.
10. Yamaguchi, T.F.; Jing, S. Bull. Chem. Soc. Jpn. **1992**, *65*, 1866–1870.
11. Rodrigues, C.A.; Reynaud, F.; Sadler, E.; Drago, V. J. Liq. Chrom. & Technol. **1999**, *22*, 761–769.
12. Colina, M.; Ledo, H.; Gutiérrez, E.; Villalobos, E.; Marín, J. J. Chromatogr. A. **1996**, *739*, 223–227.
13. Smith, R.M.; Martell, A.E. *Critical Stability Constants*; Plenum Press: New York, 1975; Vol. 2, 215.
14. Langmuir, I. J. Am. Chem. Soc. **1918**, *40*, 1361–1403.
15. Antico, E.; Masana, A.; Salvadó, V.; Hidalgo, M.; Valiente, M. J. Chromatogr. A. **1995**, *706*, 159–166.

Received May 20, 2000
Accepted October 19, 2000
Manuscript 5311