International Journal of Science and Engineering (IJSE)
Home page: http://ejournal.undip.ac.id/index.php/ijse

Study Adsorption Desorption of Manganese(II) Using Impregnated Chitin-Cellulose as Adsorbent

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Abstract - *Study adsorption desorption of manganese(II) using impregnated chitin-cellulose as adsorbent has been carried out. Chitin was extracted from snail shell and cellulose isolated from rice straw. Chitin and cellulose were impregnated using thiourea as impregnant agent. Characterization of chitin and cellulose was performed using FTIR spectroscopy, determination of water content, and ash content, while impregnated chitin-cellulose was characterized using FTIR spectrophotometer and X-Ray diffractometer. The adsorption of Mn(II) on impregnated chitin-cellulose was studied through determination of adsorption time and the influence of Mn(II) concentration, while desorption was carried out sequentially using various reagents. The results shown that chitin and cellulose from extraction processes are has similar FTIR spectrum compared to chitin and cellulose standard. The FTIR spectrum of impregnated chitin-cellulose shows both vibration of chitin and cellulose appeared and indicated successfully impregnate. These results were also equal to XRD pattern analysis. The water and ash contents of chitin are 0.038% and 0.043 while for cellulose are 0.184 % and 0.165 %, respectively. The adsorption of Mn(II) on chitin and cellulose are quite similar kinetically, while adsorption of Mn(II) on impregnated chitin-cellulose is higher at the same time with chitin and cellulose. In the low concentration of Mn(II), adsorption phenomena are similar on chitin, cellulose, and impregnated chitin-cellulose. Desorption process of Mn(II) on the adsorbents shows sodium etilenediamine tetra acetate able to desorp Mn(II) up to 68% higher than other reagents.*

Keywords: *Manganese(II), Chitin, Cellulose, Impregnated Chitin-Cellulose*

Submission: November 9, 2014 Corrected : March 8, 2015 Accepted: March 28, 2015

Doi: 10.12777/ijse.8.2.104-108

*[**How to cite this article**: Lesbani, A., Turnip, E.V., Mohadi, R., Hidayati, N. (2015).* Study Adsorption Desorption of Manganese (II) Using Impregnated Chitin-Cellulose as Adsorbent, *International Journal of Science and Engineering,* Vol. 8(2), 104-108, **Doi**: 10.12777/ijse.8.2.104-108*]*

INTRODUCTION

Adsorption is one of the useful methods for reducing heavy metals contaminant in the environment. Precipitation, ion exchange, coagulation, filtration, and other physical and chemical method also available but the precision of adsorption methods is better than others. On the other hand, an adsorption method has several advantages such as simple equipment, time efficient, easy procedure, low cost, and no contaminant effect for human and animals [1].

In the adsorption method, selection of adsorbent is vital due to efficiency adsorption process, which is indicated from adsorption capacity or adsorption percentage. There are two kinds of adsorbent that usually used in adsorption process i.e. organic adsorbent and inorganic adsorbent. Organic adsorbent such as chitin, chitosan, cellulose, and biomass are used for metal ion adsorption due to availability of functional groups of the materials. These functional groups act as donor electron or ligand, which can give electron to bind with metal ion. Another adsorbent, inorganic material such as zeolite, silicate, carbon active and porous materials can adsorb metal ion from solution through the pore of these materials. Recently the development of various adsorbent is sharply increased including modification of adsorbent by physical or chemical method.

One of the interesting adsorbent is chitin and cellulose, which are classified as organic adsorbent. Several merits of this material are naturally available, cheaper, easy to handle, and non-toxic material. Chitin can be extracted from shell of several moluscas and cellulose can be found in many plant and woods. Kartal *et.al* [2] reported heavy metal ion can be decreased using larva shell. Similar experiment was carried out by Yan and Viraraghavan [3]. which used biomass to treat heavy metal ion. The experiment indicated also the excellent results for removing heavy metal ion was obtained using cellulose and modified cellulose as adsorbent [4]. Both chitin and cellulose able to adsorp metal ion as separated adsorbent by their natural functional groups. Chitin and cellulose also can be combined together as one adsorbent with high functionality group by impregnation process. In this research we report the impregnation process of chitin onto cellulose using thiourea as impregnant in base condition. Thus impregnated chitin-cellulose was used to adsorp of manganese(II) ion. Several factor in the adsorption of manganese(II) was studied such as time of adsorption and concentration of manganese(II). At the end of experiment, desorption process was carried out sequentially to study the typical binding mechanism of metal ion onto adsorbent. Desorption process was conducted using several desorption reagents represented by physical or chemical type of adsorption.

MATERIALS AND METHODS

Materials

Chemical reagents were used in this research were analytical grade from Merck, Germany and used directly after purchased such as sodium hydroxide, hydrochloric acid, methanol, manganese(II) chloride, and thiourea. Purewater was purified using water purification apparatus. The Snail shell was obtained from low land area around Indralaya and rice straw from Pagar Alam, South Sumatera. Analysis and characterization using FTIR spectrophotometer Shimadzu 8201PC and atomic absorption spectrophotometer type JSM 6360 LA.

Extraction Chitin From Snail Shell (*Achatinafulica*) and Characterization

Snail shell was washed with water and dried after sampling. Dried shell was grounded using pestle mortar to be powder, whereas pass through 100 mm sieve. Shell powder (150 g) was mixed with hydrochloric acid 1 M, 450 mL in 1 L Beaker glass. The mixture was stirred for 30 min and filtrated to obtain residue. Residue was washed several times with water until pH 7 and dried 60 ^{o}C for 4 h. Dried residue (100 g) was added into 1 M, 500 mL sodium hydroxide in 1 L Beaker glass and stirred for 2 h under temperature 65 ^{o}C. The mixture is filtrated and residue was collected. Residue was washed with water several times until pH 7 and dried in oven to obtain white powder. White powder was chitin and characterized using FTIR spectrophotometer, water and ash contents.

Extraction Cellulose From Rice Straw and Characterization

Rice straw was grounded using pestle and mortar to be powder and pass through 60 mm sieve. The powder was place into 2 L bottle and methanol was added for 1.5 L. The mixture was kept for 2 d. Methanol was changed every 2 d until clearly color, then the mixture was filtered and residue was washed with water until pH 7. Residue was dried in oven at temperature 65 ^{o}C. Dried residue was place in 1 L Beaker glass and 400 mL, 5% hydrochloric acid was added. The mixture was stirred using magnetic stirring for 3 h, then filtered. Residue was washed with water and dried at temperature 65 ^{o}C. The residue is white brownish powder and characterized using FTIR spectrophotometer, water and ash contents.

Impregnation Chitin-Cellulose and Characterization

Chitin-cellulose material was prepared according to procedure from Khan *et.al* [5] with slightly modification. Cellulose (4 g) was added into sodium hydroxide 100 mL, 1.5 M. The mixture was stirring at room temperature for 1 h, then thiourea 300 mL, 0.65 M was added slowly. The mixture was stirring for 1 h and gel was formed. Gel was kept at 0 ^{o}C for 8 h to be reagent A. Chitin (10 g) was added into sodium hydroxide 8 mL, 46% at 0 ^{o}C. The mixture was stirred for 6 h then 52 mL cold water was added into the solution to be reagent B. Reagent A was added into reagent B in 1000 mL Beaker glass equipped with magnetic stirring. The mixture was stirred for 30 min and wash with sulphuric acid to be solid material. Solid material was washed with water and dried at 65 ^{o}C. Characterization was carried out using FTIR spectrophotometer and X-Ray diffractometer.

Adsorption of Manganese(II)

Effect of reaction time in the manganese(II) adsorption

Impregnated chitin-cellulose (0.1 g) was interacted with 10 mL of manganese(II) ion with concentration 20 mg/L using batch shaker system. The interaction time for adsorption is 10, 30, 60, and 120 minutes then filtrated. The filtrate was analyzed using atomic absorption spectrophotometer. Similar procedures are repeated by changing impregnated chitin-cellulose as adsorbent to cellulose and chitin.

Effect of concentration of manganese(II) in the adsorption

Impregnated chitin-cellulose (0.1 g) was interacted with 10 mL of manganese(II) ion using batch shaker system at room temperature for 60 minutes. Variation of concentration of manganese(II) ion is 5, 10, 50, and 100 mg/L. Filtrate after shaker was analyzed using atomic absorption spectrophotometer. The procedure above was carried out also for cellulose and chitin in similar condition with impregnated chitin-cellulose.

Desorption of manganese(II) ion

Chitin (1 g) was interacted with manganese(II) ion in 100 mg/L for 10 mL. The mixture was shaked for 60 minutes to obtain residue and filtrate. Filtrate was analyzed using atomic absorption spectrophotometer. Residue was dried at room temperature and the solid material was divided into 4 parts with 0.2 g in each part. Desorption process was carried out by adding 10 mL of hydrochloric acid 0.1 M, Sodium EDTA 0.1 M, ammonium acetate 0.1 M and water into each solid material, respectively. The mixture is shaked for 60 minutes to obtain filtrate and residue. Filtrate was analyzed using atomic absorption spectrophotometer to obtain the concentration of manganese, which lost from solid material. Similar procedure was carried out using chitin and cellulose as control of experiment.

RESULTS AND DISCUSSIONS

Characterization of Chitin, Cellulose and Chitin-Cellulose From Impregnation

Chitin from snail shell and cellulose from rice straw were extracted by standard procedure and was characterized using FTIR spectrophotometer. FTIR spectrum of chitin is shown in Figure 1 and cellulose in Figure 2. Chitin is macromolecule based carbohydrate contain almost hydroxyl group and amide group [6]. Hydroxyl group of chitin was appeared at wavenumber 3448 cm^{-1}, while amide group at 1473 cm^{-1}. These wevenumbers are found in Figure 1 with high intensity. Another group that appear in the chitin is methylene (-CH_2-), which found at wavenumber 2978 cm^{-1}. On the other hand, specific wavenumber for cellulose is only hydroxyl, which can be clearly seen at wavenumber 2924 cm^{-1} as shown in Figure 2. Water content is related with life storage of material and ash content indicated purity of compounds. Data of chitin and cellulose in Table 1 show water and ash contents for chitin and cellulose is less than 1%. This is indicated chitin and cellulose from extraction process can be used safely for impregnation. Impregnation used thiourea as agent. Impregnated chitin-cellulose was identified using FTIR spectrophotometer as shown in Figure 3. To know the quality of chitin and cellulose from extraction process, we measure water and ash contents of chitin and cellulose as presented in Table 1.

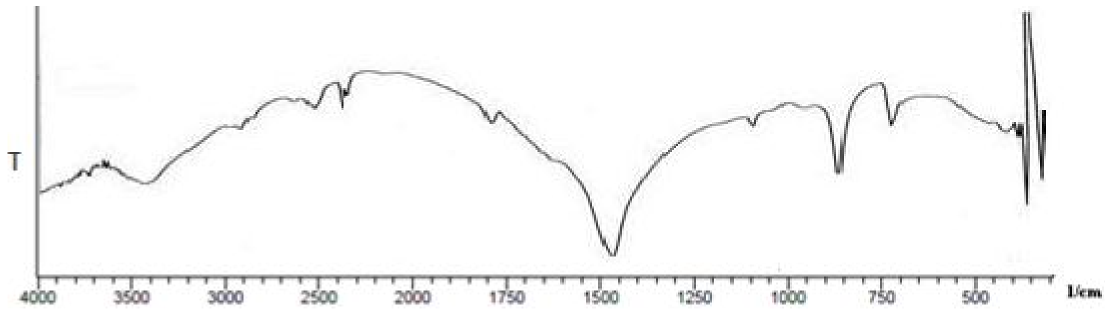

Fig. 1. FTIR spectrum of chitin from snail shell

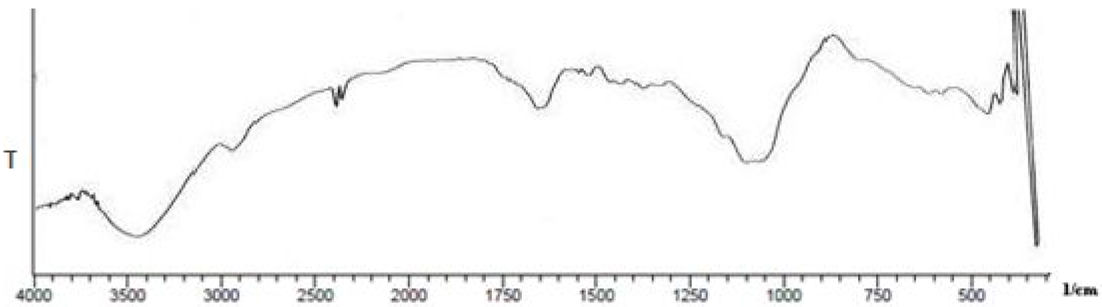

Fig 2. FTIR spectrum of cellulose from rice straw

Table 1. Water and ash contents in chitin and cellulose

Adsorbent	Water content (%)	Ash content (%)
Chitin	0.038	0.043
Cellulose	0.148	0.165

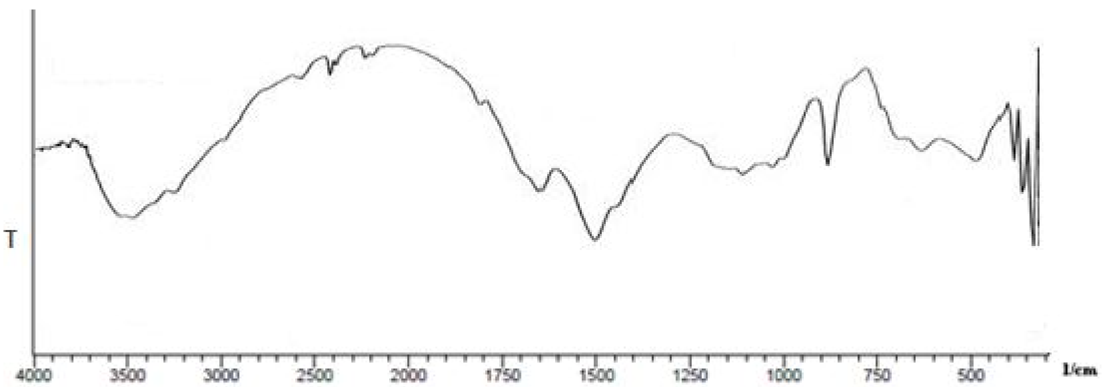

Fig.3. FTIR spectrum of impregnated chitin-cellulose

FTIR spectrum in Figure 1 and 2 was compared with Figure 3. In Figure 3, we found all vibration specific for chitin and cellulose was appeared although peaks with low vibration tape indicated impregnation process was occurred. Therefore, another characterization was carried out to know well interaction between chitin and cellulose was done. XRD data is powerful characterization to answer this research and the data is presented in Figure 4.

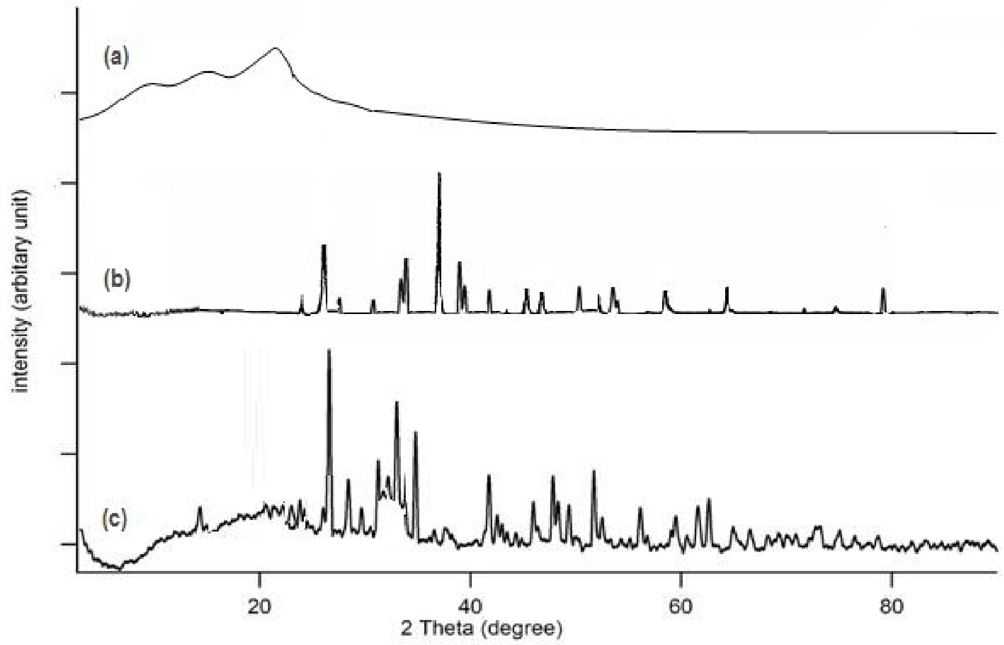

Fig 4. XRD pattern of (a) cellulose, (b) chitin, and (c) impregnated chitin-cellulose.

XRD pattern of chitin as shown in Figure 4 show similarity with standard pattern from Joint Committee on Powder Diffraction Standard (JCPDS) [7]. There are two kinds of cellulose in commercial source i.e. cellulose with high crystallinity and amorphous cellulose [8]. Figure 4 shows cellulose in this research, which extracted from rice straw is amorphous cellulose type. Impregnation process between chitin and cellulose was carried out using thiourea as impregnation agent. XRD pattern of impregnated chitin-cellulose is presented also in Figure 4. Specific pattern of chitin and cellulose was appeared in impregnated chitin-cellulose at 2θ diffraction 0-20 for cellulose and 30-40 for chitin. Thus impregnation of chitin with cellulose was successfully carried out and can be used as adsorbent in the adsorption of manganese ion.

Study Adsorption of Manganese(II)

The influence of time of adsorption using impregnated chitin-cellulose, chitin, and cellulose as adsorbents in the adsorption of manganese is presented in Figure 5. Adsoption of manganese using impregnated chitin-cellulose show highest amount compared with chitin and cellulose. By using Langmuir-Heinselwood equation [9], we obtained rate adsorption constant for adsorption of manganese using impregnated chitin-cellulose, chitin, and cellulose as adsorbents. Rate adsorption constant for impregnated chitin-cellulose, chitin, and cellulose were 0.011, 0.009. and 0.008 min^{-1}, respectively. These results indicated that reactivity of manganese increased in the adsorption using impregnated chitin-cellulose. Adsorption of manganese was also investigated by the influence of initial concentration of manganese as shown in Figure 6.

Adsorption of manganese at lower initial concentration of manganese shows similarity phenomena for all adsorbents. The adsorption process is quietly different by increasing concentration of manganese especially for chitin as adsorbent. By using Langmuir equation, we obtained adsorption capacity from data in Figure 6. Adsorption capacity for impregnated chitin-cellulose, chitin, and cellulose as adsorbents is $62.5x10^{-7}$, $55.6x10^{-7}$, and $23.3x10^{-7}$ mol/g, respectively. From this data we found that effect of time and effect of initial concentration of manganese using impregnated chitin-cellulose has similar pattern. Although both parameters are different due to kinetic and thermodynamic parameters, but adsorbent of impregnated chitin-cellulose is appropriate for adsorption of manganese compare with chitin as adsorbent or cellulose as adsorbent. Therefore, we deeply investigated adsorption of manganese using impregnated chitin-cellulose as adsorbent phenomena through desorption process using unique desorption reagents.

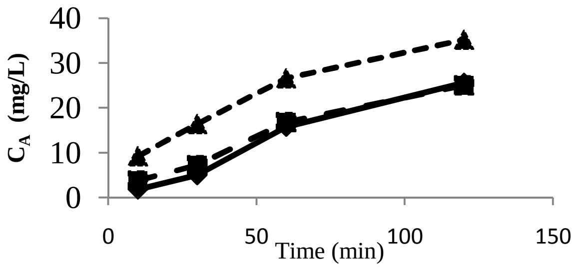

Fig. 5. Effect of time in the adsorption of manganese using chitin (♦) , cellulose (■), and impregnated chitin-cellulose (▲).

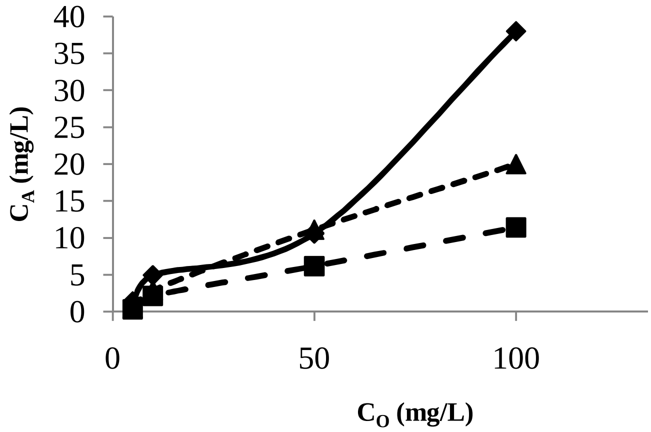

Fig. 6. Effect of manganese(II) concentration in the adsorption using chitin (♦) , cellulose (■), and impregnated chitin-cellulose (▲).

Study Desorption of Manganese (II)

Water, hydrochloric acid, sodium-EDTA, and ammonium acetate are used as desorption reagents to well known interaction between manganese and impregnated chitin-cellulose. Process investigation was performed in the first step was adsorption of manganese using impregnated chitin-cellulose then follow with desorption of manganese on impregnated chitin-cellulose. Water, hydrochloric acid, and ammonium acetate did not desorp manganese on impregnated chitin-cellulose, but sodium-EDTA can desorp manganese up to 68%. Remaining manganese 32% was still bond on adsorbent. Thus interaction between manganese with impregnated chitin-cellulose is dominated with complex formation not entrapment or acid-base interaction.

CONCLUSIONS

Chitin-cellulose was successfully impregnated using thiourea. This material can adsorp manganese(II) ion faster than adsorbent chitin and cellulose. The data of adsorption capacity shows impregnated chitin-cellulose has adsorption capacity 62.5 x 10^{-7} mol/g higher than chitin (55.6 x 10^{-7} mol/g) and cellulose (23.3 x 10^{-7} mol/g). Desorption of manganese(II) from chitin-cellulose adsorbent shows sodium etilenediamine tetra acetate can desorp manganese(II) up to 68% and higher than other reagents

ACKNOWLEDGMENT

This work was supported by Ministry of Education and Culture, Republic of Indonesia through Directorate General Higher Education (DIKTI) with “Desentralisasi Programe, Sriwijaya University” Contract No. 120/UN9.3.1/LT/2014. We also thank to Department of Chemistry, Faculty of Mathematic and Natural Sciences, Sriwijaya University for laboratory equipment in this research.

REFERENCES

[1] Longhinotti, E., Pozza, F., Furlan, L., Nazare, M.M., Sanchez, Klug, M., Laranjeira, M.C.M., and Favere, V.T., 1998, Adsorption of Anionic on the Biopolymer Chitin, *Journal of Brazil Chemistry Society*, Vol.9, No.5, 435-440.
[2] Kartal, S. N., and Imamura, Y., 2005, Removal of Copper, Chromium, and Arsenic From CCA-Treated Wood Onto Chitin and Chitosan, *Bioresource Technology,* Vol. 96, No. 3, 389–392.
[3] Yan, G., and Viraraghayan, T., 2001. Heavy Meta; Removal in a Biosorption Column by Immobilized M. Rauxil Biomass, *Bioresour Technol.* Vol. 78 No.3. 243-249.
[4] O’Connell, D.W., Birkinshaw, C., O’Dwye, T. F., 2008, Heavy Metal Adsorbents Prepared From The Modification of Cellulose: a Review, Bioresour Technol , Vol. 99, No. 15, 6709-6724.
[5] Khan, T.A., Peh, K.K., and Ching, H.S., 2002, Reporting Degree of Deacetylation of Chitosan: the Influence of Analytical Methods, *Journal of Pharmaceut Science*, 5(3):205-202.
[6] Hong, N.K., Meyer, S.P., Lee, K.S., 1989, Isolation and Characterization of Chitin from Crawfish Shell Waste, *Journal of Agriculture Food Chemistry*, 37, 575-579.
[7] Kumar, P. T. S,. Lakshmanan, V., Biswas, R., Nair, S., and Jayakumar, R., , 2012, Synthesis and Biological Evaluation of Chitin Hydrogel/Nano ZnO Composite Bandage as Antibacterial Wound Dressing, Journal of Biomedical Nanotechnology Vol. 8, 1–10.
[8] Terinte, N., Ibbett, R., and Schuster, C.H., 2011, Overview on Native Cellulose and Microcrystalline Cellulose I Structure Studied By X-Ray Diffraction (WAXD): Comparison Between Measurement Techniques, Lenzinger Berichte 89: 118-131.
[9] Oscik, J., 1982, *Adsorption,* John Wiley, Chichester.