ADSORPTION AND MODELING STUDIES OF Cr(VI) USING FULLER'S EARTH , LATERITE SOIL AND BLACK COTTON SOIL AS ADSORBENTS

Mallikarjun.S.Dengi 1 Prof. Dr. Shashikant.R.Mise 2 Prof. Saraswathi Reddy 3, Ms. Preethi 4
1Ph.D Scholar, Department of civil Engineering, PDACE, Kalaburgi, Karnataka, INDIA
2Professor PG, Department of civil Engineering, PDACE, Kalaburgi, Karnataka, INDIA
3Asst professor , Department of Civil Engineering, PDACE, Kalaburgi, Karnataka, INDIA
4M.Tech Scholar, Department of civil Engineering, PDACE, Kalaburgi, Karnataka, INDIA

---***---

Abstract - *In this research, adsorption of Chromium (VI) ions on Fuller's earth, Laterite soil and Black cotton soil has been studied through batch adsorption techniques. The main objectives of this study are, To study physico-chemical characteristics of Fuller's earth, Laterite soil and Black cotton soil. Detection of Cr (VI) removal by adsorbents as a function of contact time, adsorbent dosage and pH. To study sorption kinetics, column tracer experiment and iso thermal patterns. The obtained results of column tracer experiments for Cr (VI) adsorption are best fitted to Freundlich isotherm.*

***Key Words*: Chromium(VI), Fuller's earth, Laterite soil, Black Cotton soil and Adsorption**

1. INTRODUCTION

Modelling Adsorption properties and equilibrium data, commonly known as adsorption isotherms, describe how pollutants interact with adsorbent materials and so are critical in optimizing the use of adsorbents. In order to optimize the design of an adsorption system to remove contaminant from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. An accurate mathematical description of equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison behavior for different materials (or for varied experimental conditions) within any given system (Crini and Badot 2007, 2008).

Soil is a major reservoir for contaminants as it posseses an ability to bind various chemicals. These chemicals can exist in various forms in soil and different forces keep them bound to soil particles. It is essential to study these interactions because the toxicity of chemicals may strongly depend on the form in which they exist in the environment. Another thing is that soil variability and some environmental properties (e.g. climate factors) may change equilibrium found in soil and cause leaching of trace toxic elements like heavy metals tightly bound to soil particles. Mathematical and computer modeling help us with understanding processes occurring in soils. A number of models are being developed now which can quantitatively predict movements and sorption of heavy metals in soil with good accuracy The Mathematical modeling of the adsorption phenomena involves equilibrium isotherm models, adsorption kinetics models and controlling mechanisms models that may include external diffusion, pore diffusion and intraparticle diffusion

Chromium is the heavy metal selected in this study as an adsorbate, because of its relevance in electroplating, coating, and tanning industries. The effluents from these industries may contain detrimental concentrations of chromium

1.1 Objective of Study

1. To evaluate a feasible and economical low cost treatment of heavy metals, as present in synthetic sample by Black cotton soil, Laterite soil and Fuller's Earth which are naturally available as an adsorbent.
2. To study the physical properties of adsorbents like Black cotton soil, Laterite soil and Fuller's Earth.
3. Adsorbing capacity of Black cotton soil, Laterite soil and Fuller's Earth on adsorption of Cr as a function of contact time, adsorbent dosage and pH.
4. Sorption kinetics, Isothermal patterns, Recycle and Reuse of adsorbents
5. To study column tracer experiments.
6. Modeling study.

1.2 Modeling Study

Mathematical modeling is the major tool to predict the mobility and the persistence of pollutants to and within groundwater systems. Several comprehensive institutional models have been developed in recent years for this purpose. However, evaluation procedures are not well established for models of soil-water flow and chemical transport. The models may be used to determine the potential concentrations at receptor points and the necessity & immediacy of remedial action. The factors and processes that are important include those that affect losses, retardation, solubility and transport. For protection of public health and the environment, particularly groundwater, it is desirable to enhance losses and retardation.

There is no doubt that mathematical modeling is an invaluable tool for the analysis and design of adsorption systems and also for the theoretical evaluation and interpretation of thermodynamic parameters (Allen et al. 2004). However, two important points must be pointed out. The first is that, although these adsorption and kinetic models remain a useful and convenient tool for the comparing results from different sources due to their highly idealistic simplicity, a given plot is an empirically relationship (Liu and Liu 2008; Liu and Wang 2008; Lin and Wang 2008; Wu et al. 2009; Rudzinski and Plazinski 2009; Douven et al. 2015). An isotherm may fit experimental data accurately under one set of conditions but fail entirely under another. No single model has been found to be generally applicable. This is readily understandable in the light of the hypotheses associated with their respective deviations. In addition, the two-parameter isotherm model such as the Langmuir and theFreundlich models are based on the hypothesis of physical adsorption. In the case of dye adsorption onto a biosorbent, which is more chemical than physical, it would be more appropriate to consider pollutant adsorption with models based on chemical reactions.

However, these models are complicated in nature. Simple kinetic models used in the literature are also questionable because, generally speaking, these models cannot represent the real course of adsorption and thus cannot offer useful information to gain insight in mechanism. It is more reasonable to interpret the kinetic data in term of mass transfer (homogeneous diffusion model, double exponential model, etc.) but these models are also complex and effective graphical analysis software are required to solve mathematical models. The book published by Tien (1994) can be consulted on this topic. The second point is related the abundant literature data. Despite the number of papers published, there is as yet little literature containing a full study comparing various models and this topic clearly needs further detailed research (Wase and Forster 1997; McKay 1999; Cooney 1999; Yang 2003; Hamdaoui and Naffrechoux 2007a, b; Crini and Badot 2007, 2010).

2. MATERIALS AND METHODOLOGY

Fuller's Earth: It is a clay material that has the capability to decolorize oil or other liquids without chemical treatment. Fuller's earth typically consists of Attapulgite or Bentonite. Modern uses of fuller's earth include absorbents for oil, grease, and animal waste (cat litter) and as a carrier for pesticides and fertilizers. Minor uses include filtering, clarifying, and decolorizing; active and inactive ingredient in beauty products; and as a filler in paint, plaster, adhesives, and pharmaceuticals as shown in the below fig1 and fig 2 in solid form and powdered form respectively.

Fig- 1: Solid Form Fig- 2: Powdered Form

Laterite soil: Laterites are soil rich in iron and aluminum, formed in hot and wet tropical areas. Naturally all laterites are rusty red as shown in the fig 3 and fig 4 in solid form and in powdered form respectively. It's mainly because of iron oxides. They develop by intensive and long lasting weathering of the underlying parent rock. Tropical weathering (laterization) is a prolonged process of mechanical and chemical weathering which produces a wide variety in the thickness, grade, chemistry and ore mineralogy of the resulting soils.

Fig-3: solid form Fig- 4: powdered form

Black cotton soil: Generally, black cotton soil is found in the central, western and southern states of India, including Karnataka. Black cotton soil is one of major soil deposits of India. Black soil in India is rich in metals such as Iron, Magnesium and Aluminum. However, it is deficient in Nitrogen, Potassium, Phosphorous and Humus. as shown in the below fig 5 and fig 6 in solid form and powdered form respectively.

Fig-5: Solid form Fig-6: Powdered form

The Physico-chemical Characteristics of the adsorbents is described in the table- 1.

Table-1 physico-chemical characteristics of the adsorbents.

Sl.NO	Characteristics	Units	Fuller's Earth	Laterite Soil	Black Cotton Soil
1	Moisture Content	%	2.22	3.44	5.86
2	Decolorizing Power	mL/g	13.5	18	21
3	pH values	- - -	7.8	7.6	7.1
4	Specific Gravity	- - -	1.88	2.40	2.54
5	Surface Area	m^2/g	750	453	520
6	Bulk Density	g/cc	0.923	1.140	1.105
7	Color	- - -	Light gray	Red	Black

PREPARATION OF SYNTHETIC CHROMIUM (VI) SOLUTION

Potassium dichromate ($K_2Cr_2O_7$) is used as the source for Chromium stock solution. All the required solutions are prepared with analytical reagents and double-distilled water.2.835 g of 99% $K_2Cr_2O_7$ is dissolved in distilled water of 1 L volumetric flask up to the mark to obtain 1000 ppm (mg/L) of Cr(VI) stock solution. Synthetic samples of different concentrations of Cr(VI) are prepared from this stock solution by appropriate dilutions. For example, 10 mg/L Chromium stock solution is prepared by diluting 10 mL of 1000 mg/l Chromium stock solution with distilled water in a 1000mL volumetric flask up to the mark.

Method of Analysis:

All the glass wares used in the experimental work are soaked overnight in a 10mg/L of Chromium (VI) solution to minimize the possibility of Chromium being adsorbed on glass surface during the experimental work. The excess of Chromium is washed off with 1:3 HNO3 and distilled water prior to use. After completion of the experimental work the glassware is soaked in 1:3 HNO_3 followed by distilled water for 4hrs to remove excess Chromium and then washed with tap water before soaking in 10mg/L of Chromium (VI) solution.

3. BATCH ADSORPTION STUDY

3.1 Selection of optimum contact time:

The adsorption is strongly influenced by the contact time, for the study of effect of contact time 100mL of 10mg/L Chromium (VI) solution is mixed with 1gm of adsorbents and stirred on Gyro shaker for various time interval such as 10,20,30,40,50,60,70,80,90,100,110,120 min.

The samples are filtered and analyzed for Cr (VI) concentrations using spectrophotometric method and Atomic adsorption method respectively.

3.2 Determination of Optimum Dosage

To determine the optimum dosage of adsorbent, various dosages of adsorbents are added to the conical flask containing known concentration of Cr (VI) solutions (10mg/L).

The solution in the conical flask was subjected to stirring for optimum contact time and the dosage varies from 200 ,400, 600, 800, 1000, 1200, 1400, 1600, 1800, 2000mg. Filtered and analyzed for residual and removal of Cr (VI) concentrations. The dosage which gives minimum residual concentration is chosen as optimum dosage.

3.3 Determination of Optimum pH:

To determine the optimum pH series of conical flasks were taken with 100 mL of 10 mg/L Cr (VI) solutions. Optimum dosage of adsorbents are added to the respective flasks. The pH of the flasks are adjusted ranging from 2,3,4,5,6,7,8. The flasks were shaken for optimum contact time. After stirring, the samples are filtered and analyzed for the residual Cr (VI) concentration. The two flasks i.e. Containing Cr (VI), which gives minimum residual concentration is selected as the optimum pH.

4. RESULTS AND DISCUSSION

4.1 Determination Of Optimum Contact Time:

For the study of effect of contact time 100mL of 10mg/L Chromium (VI) solutions are taken in 250mL conical flasks respectively and mixed with 1gm of adsorbents for all the flasks and stirred on Gyro shaker for various time interval such as10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110,120 min. The samples are filtered and analyzed for Cr(VI) residual concentrations using UV visible spectrophotometric and Atomic absorption methods respectively. Contact time has greater role in the adsorption process. Percentage of Cr(VI)) removal versus time are plotted. From the figures it is observed that after equilibrium further increase in time, there is not much increase in adsorption. The removal efficiency of Chromium (VI) by Laterite soil, Black cotton soil and Fuller's Earth are found to be 88.5%**,** 70%, and 74% with optimum contact time of 70 minutes,90 minutes , 80 minutes respectively.

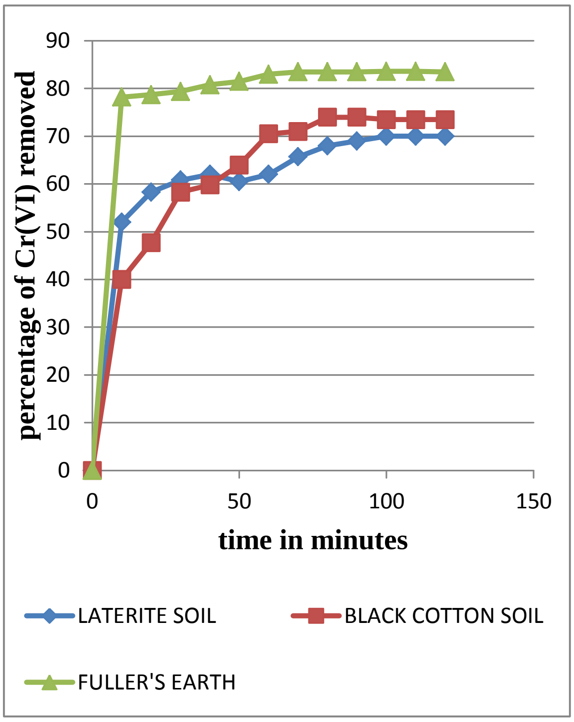


Chart-1 Effect of Contact Time on Cr(VI) Removal by Laterite soil ,Black cotton soil and Fuller's Earth

Determination of Optimum Dosage

To determine the optimum dosage of adsorbent, various dosages of adsorbents are added to 100mL of 10mg/L concentration of Cr(VI) solutions in the respective 250mL conical flasks. The solution in the conical flask was subjected to stirring for optimum contact time and the dosage varies from 2,4,6,8,1,12,14,16,18,20 g/L. The sample is filtered and analyzed for residual Cr(VI) concentrations. The dosage which gives maximum removal percentage is chosen as optimum dosage. The dosage at which the maximum removal is attained, is taken as optimum dosage. After this not much change is observed even after increase in the adsorbent dosage. The optimum dosage for Cr(VI) removal by fuller's earth, Laterite soil and Black cotton soil are 800mg ,1000mg and 1200mg with the removal efficiency of 89.30%, 71% and 78% respectively.

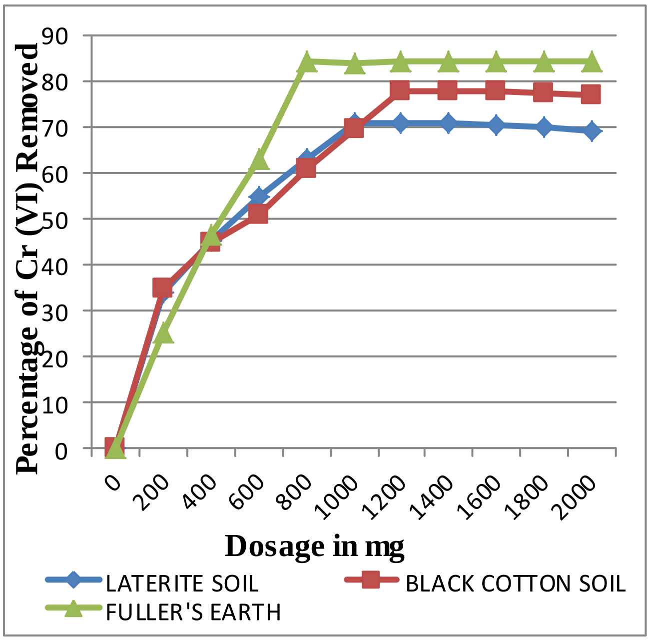


Chart-2 Effect of Adsorbent Dosage on Cr(VI) removal by Laterite soil, Black cotton soil and Fuller's Earth

Determination of Optimum pH:

To determine the optimum pH 100 mL of 10mg/L Cr(VI) solutions are taken in 250mL conical flasks respectively. Optimum dosage of adsorbents are added to the respective flasks. The pH of the flasks are adjusted ranging from 1,1.5, 2, 2.5,3,4,5, 6,. The flasks were shaken for optimum contact time. After stirring, the samples are filtered and analyzed for the residual Cr(VI) concentration. The flask i.e. Containing Cr(VI) which gives maximum removal percentage is selected as the optimum pH. It is observed that Chromium is removed more effectively in acidic range. The optimum pH for Cr(VI) removal by Laterite soil ,Black cotton soil and Fuller's earth are 1.5, 1.5 and 2 with removal efficiency of 73.0%, 76.0% and 91.5% respectively

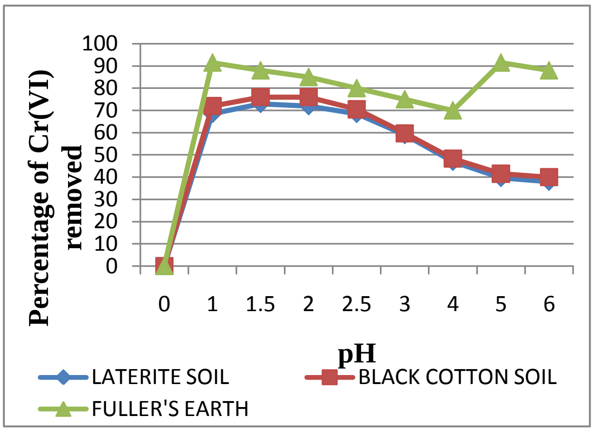


Chart-3 Effect of pH on Cr(VI) removal by Laterite soil, Black cotton soil and Fuller's Earth

Column Tracer Experiments

A series of column tracer experiments have been performed with Chromium (VI) on different adsorbents obtaining the breakthrough curves and retardation coefficients. Results obtained by Column tracer method are interpreted using Freundlich isotherm formulae describing the adsorption isotherms. In all cases of Cr(VI) adsorption, the best fit is obtained for the Freundlich isotherm, described by the formula: Cads = KF $xC_{aq}^{1/n}$ Where, Cads = balance concentration of the studied compound in the carbonbed; Caq = balance concentration of the studied compound in the water; K_F and n = coefficients of the Freundlich adsorption isotherm.

Substitute distribution coefficient (determined using the Freundlich isotherm) K_d^F for a given value of balance concentration of ion adsorbed in the solution equals

$$K_d^F = \frac{KFC_{aq}^{\frac{1}{n}}}{Caq}\, K_F C_{aq}^{(1/n-1)}$$

For the distribution coefficient determined on the basis of the adsorption isotherm, the retardation has been defined as R=1 +$\frac{\rho\, d}{n} K_d^F$

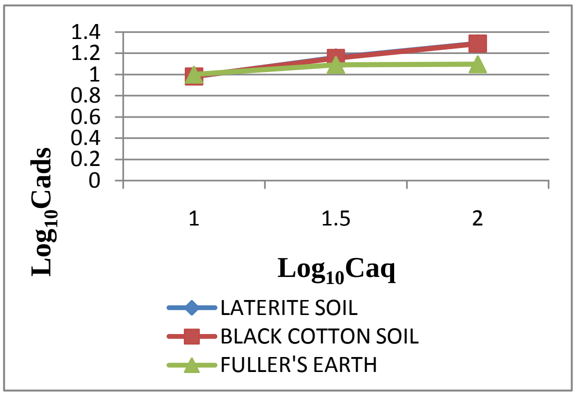


Chart-4 Adsorption of Cr(VI) for selected concentrations on different adsorbents to fit Freundlich isotherm

Single adsorption of Chromium (VI) on different adsorbents

A series of column tracer experiments for Cr(VI)have been performed on Laterite soil, Black cotton soil and Fuller's Earth. Fig.3.7, fig 3.8, fig 3.9. Shows tracer breakthrough curve for 10 mg/L of initial concentration. The results obtained with different concentrations are fit to Adsorption isotherms. Similar experiments were performed for concentration of 15 mg/L for Cr (VI) on Laterite soil, Black cotton soil and Fuller's Earth to fit Freundlich Isotherm and the respected graphs are as shown in the fig 3.6. respectively.

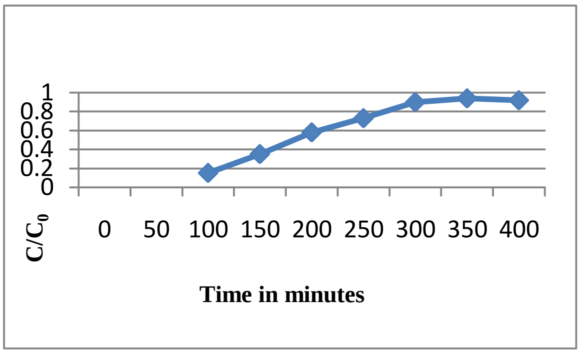


Chart-5 Break through Curve for Single Adsorption of Chromium (VI) on Laterite soil.

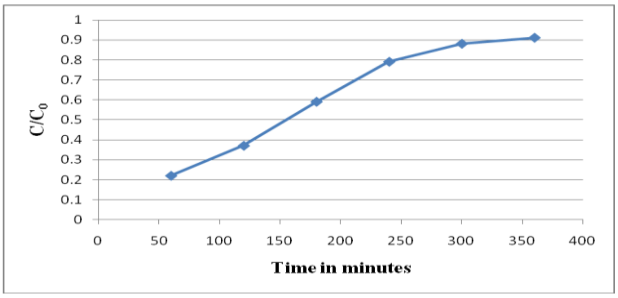


Chart-6 Break through Curve for Single Adsorption of Chromium (VI) on Black cotton soil.

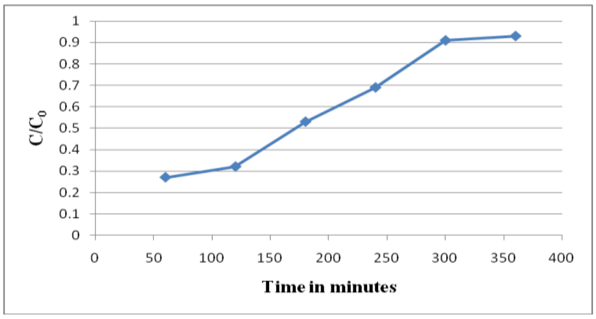
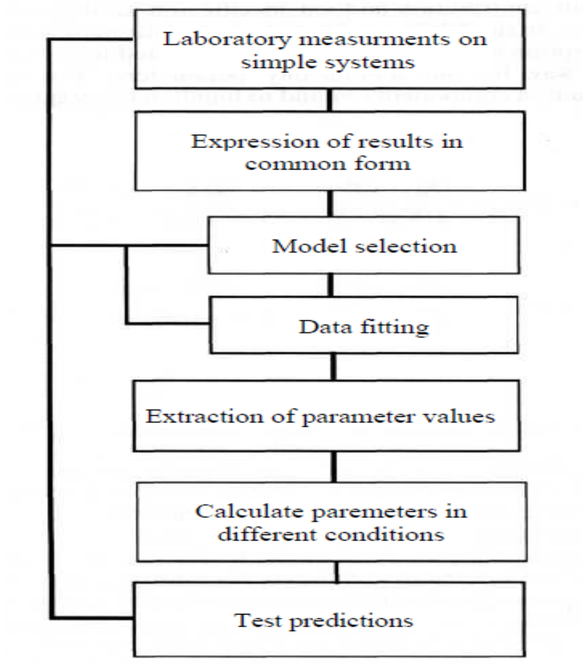


Chart-7 Break through Curve for Single Adsorption of Chromium (VI) on Fuller's Earth

The Modeling Cycle

Fig-14



KINETIC EQUATIONS

The adsorption data of Chromium are correaletedwith the following kinetic equations

1. Power function - $C_{ads} = at^b$

2. Simple Elovich equation - $Cads = C \quad + dlnK$

3. Olaofe proposed equation - $C_{ads} = \frac{K_1 t}{1+K_2 t}$

CONCLUSIONS

The data and results from the experiment reveal that removal of Chromium (VI) increases with increase in contact time and attains equilibrium at particular time. The result of experiment on optimization of dosage of adsorbent reveals that, increase in amount of dosage added, increases the removal of Chromium (VI) from the solutions. The results of batch experiments follows Freundlich isotherm (1/n<1) and proves to be a favourable adsorption. It obeys Langmuir isotherm as separation factor 'R' is lesser than 1 and greater than 0 (0<R<1). It also follows Temkin and B.E.T. isotherms.The result of the column experiments follows Freundlich isotherm (1/n< 1) indicating proves to be a favourable adsorption. The adsorptive kinetics data were satisfactorily correlated with power function, simple Elovich and Olaofe's proposed equations using linear regression analysis. The Olaofe's proposed equation was found to have the best correlation with R^2between 96-99% and the kinetics of Cr(VI) adsorption on the Adsorbents is the least when compared with other heavy metals. The Experimental result shows good removal efficiency of Chromium (VI) from their synthetic solutions by using Laterite soil, Black cotton soil and Fuller's Earth.

REFERENCES

[1] Zhe XU, Jian-guo CAI and Bing-cai PAN (February 2013) "Mathematically modeling fixed-bed adsorption in aqueous systems"*Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering) (State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, China)

[2]A. Dube, R. Zbytniewski T. Kowalkowski, E. Cukrowska and B. Buszewski (August 2000) "Adsorption and Migration of Heavy Metals in Soil" (Polish Journal of Environmental Studies Vol. 10, No. 1 (2001) 1-10)

[3]Kelvin O.Yoro, Muofhe Singo, Jean L. Mulopo and Michael O. Daramola (Novemeber 2016) "Modelling and Experimental Study of the CO_2 Adsorption Behaviour of Polyaspartamide as an Adsorbent during Post-Combustion CO_2 Capture" at School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Private Bag X3, Wits 2050, Johannesburg, South Africa.

[4]Muftah H. El-Naas* and Manal. A. Alhaija(January 2013) Chemical and Petroleum Engineering Department, United Arab Emirates University, UAE "Modelling of Adsorption processes "

[5]Y. S. HO and G. McKAY (November 1998) "A Comparison Of Chemisorption Kinetic Models Applied To Pollutant Removal On Various Sorbents" [6] D. D. Do, Adsorption analysis: equilibria and kinetics, London: Imperical College Press, 1998. [7] D. M. Ruthven, Principles of Adsorption and Adsorption Processes, New York: Wiley-Interscience, 1984.