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Review Paper

A Review and Evaluation of Selected Kinetic Models and Sorption Processes in Amended Soils

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Abstract- *The main aim is to evaluate the validity of some of the models to be used for soil systems. Soil is a major reservoir for contaminants, and it possesses an ability to bind chemical elements and compounds within its particulate mass. 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. Many researchers have been using kinetic models to simulate the adsorption process with respect to time. The study of sorption kinetics is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. In addition, kinetics models describe the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface. These soils and amended soils may be used as landfill liners; hence along with strength its sorptive or retentive capacity of these soils has to be understood. Four kinetic models namely pseudo first order, pseudo second order, Elovich and intraparticle diffusion models are reviewed to understand different soil based and non soil based adsorbents. Comparisons are made between the four kinetic models based on the published literature. Pseudo second order, Elovich and intraparticle diffusion are superior models which can be used on soil systems. The pseudo first order might not be suitable for most of the soil systems.*

Key Words: Adsorption, amended soils, pseudo first order, pseudo second order, Elovich, intraparticle diffusion etc.

Introduction

Adsorption of metal ions from aqueous solution on oxides, clay minerals and clays has been a subject of interest. It is considered that the adsorption of heavy metal ions and complexes on clay minerals occurs as a result of ion exchange, surface complexation, hydrophobic interaction and electrostatic interaction. Clay minerals play an important role in accumulation, adsorption/desorption, as well as exchange processes of metal ions. Many researchers have worked on adsorption isotherms to describe the process of adsorption taking place, generally Langmuir and Freundlich isotherms are used to describe the process of adsorption. Kinetics of adsorption is one field which many use to understand the dynamics of the adsorption reaction in terms of the order of the rate constant. Moreover, it is helpful for the prediction of adsorption rate, gives important information for designing and modelling the processes. Adsorption kinetics was modelled by the pseudo first-order, pseudo second-order rate equation, Elovich and intra-particle diffusion equations. Kinetic experiments were conducted and the data obtained was fitted on kinetic models and the adsorption kinetic rate constants were calculated respectively. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients. (*R^2*, values close or equal to 1) The relatively higher value of correlation coefficient is the more applicable model to the kinetics of heavy metal adsorption and many researchers have based their conclusions on this as it gives an easy conclusion on the validity of the model. [1,2,3]

Review of pertinent literature

[4] Gupta et al. 2009 have worked on the Indian expansive soils and its interaction with cadmium, it was found that the pseudo first order model was inadequate in explaining the experimental sorption data, however, the pseudo second order model was a good fit with the experimental data.

[5] Oladoja et al. 2008 have worked on adsorption of methylene blue on ground palm kernel coat (PKC). The ability of the PKC to remove Methylene Blue (MB), a basic dye from waste stream, was studied by the method of continuous variation of 2 process variables: Initial MB concentration (mg/l) and PKC dosage (g/l). The amount of MB sorbed per gram of PKC increased with increasing initial MB concentration while a reverse trend was observed when the PKC dosage was increased. The experimental data were fitted into the following kinetic models: Lagergren pseudo-first order, the chemisorptions pseudo-second order, Elovich kinetic model, and the intraparticle diffusion model. It was observed that chemisorptions pseudo-second order kinetic model described the sorption process with high coefficients of determination (R^2) better than any other kinetic models.

[6] Oladoja et al. 2007 worked on the use of rubber seed shell (RSS) as an adsorbent for methylene blue dye, analysis of the data obtained from the different sorption studies revealed that the data fitted better to the pseudo-second order model than any other kinetic model, indicating that the sorption process will include chemisorptions of methylene blue dye on rubber seed shell.

[7] Veli et al. 2007 have used cankiri bentonite a natural clay as an adsorbent for removal of zinc and copper from aqueous solutions,. During the removal process, batch technique was used, and the effects of pH, clay amount, heavy metal concentration and agitation time on adsorption efficiency were studied. It was determined that adsorption of Cu^{2+} and Zn^{2+} fitted well by the second order reaction kinetics. In addition, calculated and experimental heavy metal amounts adsorbed by the unit clay mass were almost same.

[8] Erika et.al 2009, have studied the kinetics for the sorption of molybdate and phosphate by four Chilean soils. Among the five kinetic models examined the Elovich equation gave the best fit of the experimental data (R^2 = 0.93 to 0.97, standard error = 0.35 to 0.94). The sorption rate constant (α) for both anions was related to the organic matter (OM) content of the soils, especially the content of Al- and Fe-humus complexes. The values for molybdate were 2.24×10^{15} mmol kg^{-1} h^{-1} for the Vilcún soil (15% OM), 2.49 $\times 10^{12}$ mmol kg-^{1} h^{-1} for the Pemehue soil (16% OM), 8.76x1010 mmol kg-1 h-1 for the Osorno soil (20% OM), and 3.11x107 mmol kg^{-1} h^{-1} for the Piedras Negras soil (24% OM). The corresponding values for phosphate were 3.89×10^{7}, 5.21×10^{10}, 3.11×10^{12} and 1.08×10^{16} mmol kg^{-1} h^{-1}. The desorption rate constant (α) for the four soils (in the above order) ranged from 0.47 to 0.28 for molybdate, and 0.22 to 0.39 mmol kg^{-1} h^{-1} for phosphate. The results suggest that the mineralogical composition and organic matter content of the Andisols control the kinetics for the sorption of both molybdate and phosphate. Molybdate appeared to have a high affinity for Fe- and Al-oxides, while phosphate was largely sorbed to Fe-and Al-humus complexes.

[9] Vladimir et al. 2008 have worked on kinetics of K release from soils of Brazilian coffee regions This study was conducted to evaluate K release rates from the whole soil, clay, silt, and sand fractions of B-horizon samples of a basalt-derived Oxisol and a sienite-derived Ultisol, both representative soils from coffee regions of Minas Gerais State, Brazil. Potassium was extracted from each fraction after eight different shaking time periods (0–665 h) with either 0.001 mol L^{-1} citrate or oxalate at a 1:10 solid:solution ratio. First-order, Elovich, zero-order, and parabolic diffusion equations were used to parameterize the time dependence of K release. For the Oxisol, the first-order equation fitted best to the experimental data of K release, with similar rates for all fractions and independent of the presence of citrate or oxalate in the extractant solution. For all the soils studied Ultisol fractions, in which K release rates increased when extractions were performed with citrate solution, the Elovich model described K release kinetics most adequately. The highest potassium release rate of the Ultisol silt fraction was probably due to the transference of “non-exchangeable” K to the extractant solution, whereas in the Oxisol exchangeable potassium represented the main K source in all studied fractions.

[10] Dimirkou et al. 1994 studied the kinetics of potassium adsorption in the soils of Central Greece. Four kinetic models namely first order, parabolic diffusion, power function and Elovich were used. It was found that only Elovich and first order rate models adequately described the adsorption of potassium onto soils.

[11] Sujatha et al. 2008 have conducted experimental and theoretical studies on orthophosphoric acid activated babul seed carbon as an adsorbent for the removal of methylene blue dye, pseudo first order, pseudo-second order and Elovich kinetic models were used to test the adsorption kinetics. First order gave dependable results at lower concentrations and at higher concentrations second order performed well, Elovich gave a good fit of the data analysed which shows it is more a chemisorption phenomenon occurring.

[12] Atef et al. 2009 have worked on phenol adsorption onto activated phosphate rocks of Jordan. The experimental data was fitted on four kinetic models namely pseudo first order, second order, Elovich and intraparticle diffusion. It was concluded that the pseudo second order could describe best the sorption kinetics than other models.

[13] Dang et al. 2009 have used iron modified rice husk carbon as an adsorbent to remove arsenic in simulated ground water. The experimental data was applied to two kinetic models namely pseudo first order and second order, they found the pseudo second order gave best fit with the experimental data obtained.

[14] Nemr 2009, has used pomegranate husk which was converted into activated carbon and tested for its ability to remove hexavalent chromium from wastewater. The ability of activated carbon to remove chromium from synthetic sea water, natural sea water and wastewater was investigated as well. The experimental data was fitted to four kinetic models like pseudo first order, second order, Elovich and intraparticle diffusion models. It was found that pseudo second order gave the best fit compared to other models studied.

[15] Lian et al. 2008 have used Ca- bentonite adsorbent to remove congo red colour, experimental data was fitted on three kinetic models (Pseudo first and second order followed by intraparticle diffusion). It was found that, pseudo second order gave a better fit for all the samples considered.

[16] Biplob etal. 2010 studied selenite adsorption on Zr^{IV}-loaded orange waste gel. The experimental data was fitted to pseudo first order, second order and intraparticle diffusion models, pseudo second order was found to characterize the adsorption kinetics for all the initial selenium concentrations tested.

[17] Atmani et al. 2009 have worked on use of treated and natural skin almonds to sorb methyl orange and crystal violet dyes; the experimental data was fitted on pseudo second order and intraparticle diffusion. Pseudo second order was better in describing the adsorption process and intraparticle diffusion proved along with adsorption diffusion was also a major phenomenon.

[18] Ho &Mc Kay 1999, have done a detailed literature review of more than 70 systems ,since 1984 and over 43 of these reported the mechanism as being a pseudo-first order kinetic mechanism. Three sorption kinetic models have been used to test 11 of the literature previously reported as first order kinetics and one system previously reported as a second order process. In all 12 systems, the highest correlation coefficients were obtained for the pseudo-second order kinetic model. For all of the systems studied, chemical reaction seems significant in the rate-controlling step and the pseudo-second order chemical reaction kinetics provide the best correlation of the experimental data, whereas the pseudo-first order model proposed fits the experimental data well for an initial period of the first reaction step only. However, over a long period the pseudo-second order model provides the best correlation for all of the systems studied. The following table 1 gives a comparison of all the papers considered.

Theories of Kinetic Modeling

Pseudo first-order kinetic model

The kinetic data were treated with the first-order model, which is the earliest known one describing the adsorption rate based on the adsorption capacity. It is generally expressed as follows:

$$\frac{dqt}{dt} = K_1(q_e - q_t) \qquad [1]$$

where qe and qt are the adsorption capacity at equilibrium and at time t, respectively (mg g−1), and k_1 is the rate constant of pseudo first-order adsorption (min−1). Eq. (1) was integrated with the boundary conditions of t=0 to $t = t$ and $q_t = 0$ to $q_t = q_t$ and rearranged to the following linear equation:

$$Ln(q_e - q_t) = Lnq_e - k \qquad [2]$$

If the pseudo first-order kinetics was applicable, a plot of log ($q_e - q_t$) versus t should provide a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively. The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process.

Pseudo second-order kinetic model

Adsorption kinetic was explained by the pseudo second-order model is as follows:

$$\frac{dqt}{dt} = K_2\,(q_e - q_t)^2 \qquad [3]$$

where k_2 (gmg^{-1} min^{-1}) is the second-order rate constant of adsorption. Integrating Eq. [3] for the boundary conditions q=0 to $q = q_t$ at t=0 to $t = t$ was linearized to obtain the following equation:

$$\left(\frac{t}{q_t}\right) = \frac{1}{K_2\ q_e{}^2} + \frac{1}{q_e}(t) \qquad [4]$$

The plot of t/q_t versus t should show a linear relationship if the second-order kinetics is applicable. Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q_t versus t.

Elovich kinetic model

Elovich kinetic equation is another rate equation based on the adsorption capacity, which is generally expressed as

$$\frac{dq_t}{dt} = \alpha\exp\,(-\beta qt) \qquad [5]$$

Where α is the initial adsorption rate (mg g−1 min−1) and β is the desorption constant (gmg−1) during any one experiment. It is simplified by assuming $\alpha\beta t \gg t$ and by applying the boundary conditions $qt = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. [5] becomes as followed:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad [6]$$

If heavy metal adsorption fits the Elovich model, a plot of qt versus $\ln(t)$ should yield a linear relationship with a slope of $\left(\frac{1}{\beta}\right)$ and an intercept of $(1/\beta) \times Ln(\alpha\beta)$ Thus, the constants can be obtained from the slope and the intercept of the straight line.

The intraparticle diffusion model

The adsorption process requires a multi-step approach involving the transport of solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process, and is therefore, rate- determining step. The intraparticle diffusion model is explored by using the following equation

$$q_t = K_{dif}\ t^{\,0.5} + C \qquad [7]$$

where C is the intercept and K_{dif} (mg g^{-1} $min^{-0.5}$) is the intraparticle diffusion rate constant. The plot of qt against $t^{0.5}$ may present a multi-linearity correlation, which indicates that two or more steps occur during adsorption process . The rate constant K_{dif} is directly evaluated from the slope of the regression line and the intercept is C. [2]

Table 2 gives details of different linear forms of models used and their procedure for applying it to experimental data.

Material and Methods

In order to test these models on local and amended soils, experiments were conducted and this data was fitted on the models as discussed above. Red soil of Bangalore and black cotton soil of Belgaum, Karnataka state, India were selected as the main soil for study. Further it was amended with lime, cement and flyash obtained from Raichur Thermal Power Station, (RTPS), Raichur, Karnataka. These sorbents were to be tested for their probable use as a liner material for waste containment facilities. Copper and hexavalent chromium were used as heavy metals, which will act as solute to these sorbents.

Kinetic studies were done by shaking 5 grams of adsorbent in 100 ml of solution maintaining a S/L ratio (solids to liquid ratio) of 1:20 and adding heavy metals in different concentrations of 10, 20 30 and 40 mg/l at room temperature. Samples of 5 ml were collected at required intervals and centrifuged for 5 minutes. The clear solutions were analysed for residual heavy metal concentration in the solution. The concentration of heavy metals for kinetic studies was measured using atomic absorption spectrophotometer supplied by Perkin Elmer Corp AA200 Model. [2]

Results and Discussion

Time dependent kinetic experiments were conducted for 24 hours period and samples drawn at regular intervals and their concentrations were analyzed. It was found that for both copper and chromium within 200 minutes maximum sorption occurred and over a period of 24 hours complete sorption took place. [19]

Pseudo first and pseudo second order kinetic models.

The experimental results obtained were fitted in the kinetic models as discussed earlier, table 3 and 4, represents the parameters calculated from both the models. It can be seen that for pseudo first order model the rate constants for both red soil and black cotton soil were not consistent and no relationship can be derived, which proves pseudo first order model was not suitable. Even though, the correlation coefficient for red soil and black cotton soil shows good linearity. Similarly from table 3 and 4 it can also be seen that the rate constant obtained through pseudo second order kinetic model was more consistent and varies inversely with increase in initial concentration the reason may be as the rate of reaction decreases the reaction reaches its completion with most of the reactants forming into products which might not be the case at a higher rate of reaction. [20]

This was also observed experimentally as maximum adsorption took place at a higher initial concentration. Pseudo second order kinetic model shows higher linearity compared to first order also the degree of linearity was higher in black cotton soil than red soil. Many researchers have based their conclusions only on the value of coefficient of correlation (R^2). If the R^2 value is closer to 1 the model is regarded as best fit. The above data suggests that for all the soils and amended soils taken, pure adsorption was not the only process taking place instead many other processes like precipitation, ion exchange are also dominant in this heterogeneous system of soils and amended soils.[21]

Standard error of estimate (SEE)

In order to compare the accuracy of these two models a statistical method was used to ascertain which model was more accurate. The model calculated values of sorption coefficient and experimental values for both the models showed variation, in order to access which model was better in terms of accuracy, this statistical method gives us a better idea. The standard error of estimate is a measure of the accuracy of predictions the standard error of estimate (SEE) is defined by

$$SEE = \sqrt{\frac{(\sum Qexp - \sum Qthe)^2}{(n-2)}} \quad [8]$$

Where Q_{exp} and Q_{the} are the respective experimental and model estimated sorption coefficients, n is the number of observations and (n-2) is used because two parameters (the slope and the intercept) were estimated in order to estimate the sum of squares. Also it has been reported that lower the SEE value higher is the accuracy. [9]

By observing table 5 it can be seen that pseudo second order's SEE values are lower than pseudo first order, hence it can be said that pseudo second order is more accurate than first order. Or pseudo second order is a better model when compared to first order for these mixtures.

Elovich kinetic model

From table 6 and 7 correlation coefficients obtained by Elovich model showed good linearity. It can also be observed that Elovich model gives us an account of the desorption process taking place, it can be seen from table 6 and 7 that as the initial concentration was increasing desorption (β) was decreasing in other words adsorption was increasing. This phenomenon was also seen during the experimental work, where in the sorption coefficient increased with increase in initial concentration. The reason might be at lower concentration the competition from other ions is dominant, hence desorption is higher at lower concentration, which decreases with increase in initial concentration. The correlation coefficients obtained are almost linear which shows the model fits well. Elovich model gives a good correlation for adsorption on highly heterogeneous surfaces like soil and also it shows that along with surface adsorption chemisorptions is also a dominant phenomenon taking place.

Intra - particle diffusion model

From table 8 and 9, the value of *C* provides information about the thickness of the boundary layer, since the resistance to the external mass transfer increases as the intercept increases. R^2 values given in Table 8 and 9, do not confirm that the rate-limiting step was actually the intra-particle diffusion process for the data analyzed when the R^2 values become close to 1.000. But the linearity of the plots demonstrated that intra-particle diffusion played a significant role in the uptake of the copper and chromium by sorbent. It can be observed that both surface adsorption and intra-particle diffusion were involved in the rate-limiting step. However, still there is no sufficient indication about which of the two steps was the rate-limiting step. It has been reported that if the intraparticle diffusion is the sole rate-limiting step, it is essential for the qt versus $t^{1/2}$ plots to pass through the origin, which is not the case in this.

Conclusion

In this paper an effort has been made to compare four kinetic models in order to ascertain their validity on soil systems. 15 sorbents were taken from literature and evaluated, it was found that 11 of the systems satisfy pseudo second order and 4 satisfy Elovich model. Similarly 10 sorbents of soils and amended soils were taken and kinetic studies were done, it was found that all satisfy pseudo second order. It has been found that at low concentrations of solute, it satisfies pseudo first order as the concentration increases pseudo second order fits well, which proves along with surface adsorption some other processes are also taking place.

Elovich gives good correlation between sorption and desorption, as the initial concentration increases desorption decreases, initial concentration and desorption are inversely related the reason might be at low concentrations competing ions might get adsorbed hence desorption is high. Intraparticle diffusion tries to classify whether along with adsorption does diffusion also plays a role, and which one is the dominant of the two. It can be concluded that in a highly heterogeneous system which is a character of soils along with surface adsorption, chemisorptions, ion exchange, precipitation and intraparticle diffusion are occurring concurrently. It was not possible to find which process was dominant. Finally from the above study it can be concluded that pseudo second order gives a fairly good idea about the process of adsorption taking place. Mathematical and computer modeling helps 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. Investigations for determining chemical properties of soil, heavy metal interactions, should continue because a lot of questions about this strongly heterogenic matrix are still not answered.

References

1. Syed Abu Sayeed Mohammed & Maya Naik,. Potential Use of Black Cotton Soil with additives as a Liner material to retain Zinc: Isotherm and Kinetic Studies. *International Journal of Ecology and Development*, **19(S11)**, 15 – 29 **(2011).**
2. Syed Abu Sayeed Mohammed, Maya Naik. Sanaulla P.F, Zulfiqar Ahmed M.N;.Studies on contaminant transport, at an Industrial waste dumpsite of Bangalore, India'. *Ambiente & Agua – An Interdisciplinary Journal of Applied Science.*, **3 (3)**,55 – 66 **(2008).**
3. Syed Abu Sayeed Mohammed , Maya Naik. Syed Tanveeruddin. Influence of additives on the retention of metal ions in a soil of Bangalore, India.

Ambiente & Agua – An Interdisciplinary Journal of Applied Science..**4 (1),**20 – 36 **(2009).**

4. K. Gupta, A.K. Singh & R. K. Srivastava;. Kinetic Sorption Studies of Heavy Metal Contamination on Indian Expansive Soil, *E-Journal of Chemistry*, **6(4)**, 1125-1132 **(2009).**
5. Oladoja.N.A.,Asia.I.O.,Aboluwoey.C.O,Olademeji. Y.B.,Ashogbon.A.O;. Studies on the sorption of basic dye by. Rubber seed shell, *Turkish .J.Eng. Env.Sci*, **32**, 143 – 152 **(2008).**
6. Oladoja.N.A.,Aboluwoey.C.O,Olademeji.Y.B;. Kinetics and Isotherm studies on Methylene Blue Adsorption onto Ground Palm Kernel Coat. *Turkish .J.Eng. Env.Sci*, **32**, 303 – 312 **(2008).**
7. Sevil Veli. Bilge Alyuz ;. Adsorption of Zinc and zinc from aqueous solutions by using natural clay.,*Journal of Hazardous Materials*. **149**,226 – 233 **(2007).**
8. Erika Marina Vistoso G., Nanthi S. Bolan, Benny. G. Theng, María de la luz Mora,. Kinetics of molybdate and phosphate sorption by some chilean andisols *J. Soil Sc. Plant Nutr*. **9 (1)**, 55-68 **(2009).**
9. Vladimir Antônio Silva, Giuliano Marchi, Luiz Roberto, Guimarães Guilherme, José Maria de Lima, Francisco Dias, Nogueira, Paulo Tácito Gontijo Guimarães;. ‘Kinetics of K release from soils of Brazilian coffee regions: effect of organic acids’. *Revista. Bras. Ci. Solo*, **32**,533 – 540 **(2008).**
10. Dimirkou, A. Ioannou,J. Mitsios, M. Doula, and CH. Deligiann;. Kinetics of potassium adsorption by etisols of Greece,.Commun. *Soil Sci. Plnt Anal.*, **25**(9&10): 1417 – 1430 **(1994).**
11. Sujatha M, Geetha A, Sivakumar P, and Palanisamy,. Orthophosphoric acid activated babul seed carbon as an adsorbent for the removal of methylene blue,*E- Journal of Chemistry*, **5(4),**742-753 **(2008).**
12. Atef S. Alzaydien & Waleed Manasreh,. Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto activated phosphate rock, *International Journal of Physical Sciences.* , **4(4)**, 172-181 **(2009).**
13. Son Van Dang ,Junjiro Kawasaki, Leonila C. Abella, Joseph Auresenia, Hiroaki Habaki ,Pag-asa D. Gaspillo, Hitoshi Kosuge, Hoa Thai Doan,. Removal of arsenic from simulated groundwater by adsorption using iron-modified rice husk carbon, *Journal of Water and Environment Technology*., **7 (2),**43 – 56 **(2009).**
14. Ahmed EL Nemr., Potential of pomegranate husk carbon for Cr (VI) removal from wastewater: Kinetic and Isotherm studies, *J of Hazardous Materials*., **161**,132- 141**(2009).**
15. Lili Lian, Liping Guo, Chunjing Guo;. Adsorption of Congo red from aqueous solutions onto Ca-bentonite, *Journal of Hazardous Materials*. , **161**, 126–131**(2009).**
16. Biplob Kumar Biswas, Katsutoshi Inoue, Hidetaka kawakita, Hiroyuki Harada, Keisuke Ohto, Shafiq Alam, Study of ZrIV-loaded Orange Waste Gel for elenate Adsorption, *Journal of Water and Environment Technology*., **8 (4)** ,313- 320 **(2010).**
17. Fatiha Atmani, Bensmaili A, Mezenner NY,.Synthetic Textile Effluent Removal by Skin Almonds waste, *Journal of Environmental Science and Technology*., **4(2)**:. 1-17**(2009).**
18. H.O. Y.S, MC Kay. G,. Pseudo – second order model for sorption processes, *Journal of Process Biochemistry*, **34**, 451 – 465**(1999).**
19. Heike.B.Bradl, Adsorption of Heavy metal ions on soils and soils constituents, *Journal of Colloid and Interface Science*. **277**, 1 -18 **(2004).**
20. Syed Abu Sayeed Mohammed and Maya Naik, Adsorption Characteristics of Metals in Aqueous Solution by Local Materials with Additives as Liners for Waste Containment Facilities, *Journal of Water and Environment Technology*. **8(1)**, 29 – 50 **(2010).**
21. Syed Abu Sayeed Mohammed, Maya Naik, Utilization of Red soils and amended soils as a liner material for attenuation of copper from aqueous solution: Isotherm and Kinetic Studies. *Journal of Environmental Science and Technology* **4(5)** 504 – 519 **(2011).**

Table 1: Comparison of mechanisms of sorption

Sorbent	Solute	Models	Reference
Indian expansive soil	Cadmium	Pseudo second order	[4] Gupta et al., 2009
Rubber seed shell (RSS)	Methylene Blue	Pseudo second order	[5]Oladoja et al., 2007
Ground palm kernel coat (PKC)	Methylene Blue	Pseudo second order	[6]Oladoja et al., 2008
Cankiri bentonite a natural clay of Turkey	Copper and Zinc	Pseudo second order	[7] Veli et al., 2007
Four Chilean soils	Molybdate and phosphate	Elovich	[8] Erika et al., 2009
Basalt-derived Oxisol soil of Brazil	Potassium	Elovich	[9] Vladimir et al., 2008
Sienite-derived Ultisol soil of Brazil	Potassium	Elovich	[9] Vladimir et al., 2008
Soils of Central Greece	Potassium	Elovich	[10] Dimirkou et al., 1994
Orthophosphoric acid activated babul seed carbon	methylene blue dye	Pseudo second order	[11] Sujatha et al., 2008
Activated phosphate rocks of Jordan.	Phenol	Pseudo second order	[12] Atef et al., 2009
Iron modified rice husk carbon	Arsenic	Pseudo second order	[13] Dang et al., 2009
Pomegranate husk converted into activated carbon	Cr^{6+}	Pseudo second order	[14] Nemr 2009
Ca- bentonite	Congo red colour	Pseudo second order	[15] Lian et al., 2008
Zr^{IV}- loaded orange waste gel	selenite	Pseudo second order	[16] Biplob et al., 2010
Treated and natural skin almonds	methyl orange and crystal violet dyes,	Pseudo second order	[17] Atmani et al., 2009

Table 2: Linear forms of Models used [3]

Sl No.	Name	Linear Form	Plot	Slope	Intercept
1.	Sorption Coefficient	$q_e = \frac{(C_0 - C_e)V}{M}$	-	-	-
2.	Pseudo First Order Kinetic Model	$Ln(q_e - q_t) = Lnq_e - k_1 t$	$Ln(q_e - q_t)$ Versus t	K_1	q_e
3.	Pseudo Second Order Kinetic Model	$\left(\frac{t}{q_t}\right) = \frac{1}{K_2\ q_e^2} + \frac{1}{q_e}(t)$	$\frac{t}{q_t}$ versus t	q_e	K_2
4.	Elovich Kinetic Model	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$	q_t versus $\ln(t)$	$\frac{1}{\beta}$	$\frac{1}{\beta}\ln(\alpha\beta)$
5.	Intraparticle Diffusion Model	$q_t = K_{dif}\ t^{0.5} + C$	qt versus $t^{0.5}$	K_{dif}	C

where

q_e Sorption Coefficient in mg/g or amount of adsorbed heavy metal per unit soil mass.

C_o Initial concentration of contaminant in mg/l.

C_e Final Concentration of contaminant in mg/l.

M mass of adsorbent in grams.

V Solution volume in ml.

q_t Amount of heavy metal adsorbed at time t in mg/g.

t time in minutes

K_1 Rate constant of Pseudo first order adsorption (min^{-1}).

K_2 Second order rate constant of adsorption ($gmg^{-1}\ min^{-1}$).

α Initial adsorption rate ($mg\ g^{-1}\ min^{-1}$).

β Desorption constant ($g\ mg^{-1}$).

K_{dif} intraparticle diffusion rate constant ($mg\ g^{-1}\ min^{-0.5}$).

C Y- Intercept if intraparticle diffusion

Table 3: Comparison of the first order and second order adsorption rate constants for different initial copper concentrations with different soils and amended soils

Red soil with copper						**Black cotton soil with copper**			
Parameters		**Pseudo first order**		**Pseudo second order**		**Pseudo first order**		**Pseudo second order**	
Sorbent	**Initial Conc. mg/l**	**K_1 per min**	**R^2**	**K_2 g/mg-min**	**R^2**	**K_1 per min**	**R^2**	**K_2 g/mg-min**	**R^2**
Soil	10	0.1295	0.8277	1972.8	0.9391	0.298	0.8277	647.44	0.908
	20	0.2481	0.9306	321.53	0.9189	0.571	0.93	1207.9	0.935
	30	0.2402	0.9653	1861.34	0.9423	1.684	0.822	572.03	0.917
	40	0.1581	0.9142	528.2	0.9374	2.619	0.793	468.95	0.939
Soil with 3%Lime	10	0.3602	0.938	1864	0.9423	2	0.825	2966	0.942
	20	2.7793	0.7737	709.25	0.9366	0.322	0.951	865.72	0.942
	30	0.8095	0.8071	619	0.9423	0.233	0.964	623.4	0.942
	40	0.4647	0.948	589.85	0.9423	2.313	0.805	449.8	0.942
Soil + 6% Lime	10	0.349	0.957	1660.8	0.937	2.244	0.801	1470.9	0.94
	20	0.301	0.897	1084	0.942	0.693	0.897	825.75	0.942
	30	0.282	0.92	684	0.942	0.193	0.976	537.75	0.942
	40	0.289	0.941	519	0.942	2.206	0.788	404.95	0.942
Soil with 1% Cement	10	0.1	0.906	1761	0.932	0.231	0.906	1590	0.936
	20	0.238	0.91	897.2	0.933	2.7	0.786	806.7	0.936
	30	1.126	0.797	618.96	0.942	0.231	0.906	550.6	0.942
	40	1.003	0.796	499	0.942	3.029	0.786	431.69	0.942
Soil with 3% Cement	10	0.245	0.907	1902	0.936	0.236	0.94	1502	0.942
	20	0.101	0.906	1097.9	0.939	0.303	0.982	798.9	0.935
	30	0.238	0.94	666.2	0.939	0.451	0.993	533.94	0.938
	40	0.132	0.901	488.3	0.931	0.214	0.964	396.23	0.942
Soil + 10% Fly Ash	10	0.095	0.944	1326.1	0.933	0.220	0.944	279.1	0.910
	20	0.213	0.947	721.6	0.933	0.190	0.947	145.0	0.904
	30	0.614	0.788	447.6	0.928	0.117	0.937	99.8	0.918
	40	0.149	0.929	329.8	0.933	0.860	0.817	260.3	0.933
Soil + 20% Fly Ash	10	0.126	0.923	1760.9	0.923	0.292	0.935	370.6	0.892
	20	0.283	0.926	958.2	0.923	0.253	0.938	192.5	0.895
	30	0.816	0.770	594.3	0.918	0.155	0.927	132.5	0.909
	40	0.198	0.907	438.0	0.923	1.142	0.809	345.6	0.923
Soil + 30% Fly Ash	10	0.125	0.914	1739.2	0.914	0.288	0.926	366.0	0.883
	20	0.279	0.916	946.4	0.914	0.250	0.929	190.2	0.886
	30	0.806	0.762	587.0	0.909	0.153	0.918	130.9	0.899
	40	0.196	0.898	432.6	0.914	1.128	0.800	341.4	0.914
Soil + 40% Fly Ash	10	0.139	0.904	1934.9	0.905	0.320	0.916	407.2	0.874
	20	0.311	0.907	1052.9	0.905	0.278	0.919	211.6	0.877
	30	0.896	0.755	653.0	0.900	0.170	0.909	145.6	0.890
	40	0.218	0.889	481.2	0.905	1.255	0.792	379.8	0.905
Soil + 50% Fly Ash	10	0.156	0.954	2174	0.942	0.36	0.954	457.5	0.919
	20	0.349	0.957	1183	0.942	0.312	0.957	237.7	0.913
	30	1.007	0.796	733.69	0.937	0.191	0.946	163.6	0.927
	40	0.245	0.938	540.7	0.942	1.41	0.825	426.7	0.942

Table 4: Comparison of the first order and second order adsorption rate constants for different initial chromium concentrations with different soils and amended soils

Red soil with Chromium						Black cotton soil with Chromium			
Parameters		Pseudo first order		Pseudo second order		Pseudo first order		Pseudo second order	
Sorbent	Initial Conc mg/l	K_1 per min	R^2	K_2 g/mg-min	R^2	K_1 per min	R^2	K_2 g/mg-min	R^2
Soil	10	0.1953	0.9061	1894	0.9377	0.567	0.986	637.28	0.92
	20	0.3732	0.9347	1657.8	0.9372	0.567	0.986	105.65	0.93
	30	0.2606	0.9125	770.73	0.9401	2.191	0.814	34.73	0.918
	40	0.2463	0.9863	868.8	0.9411	0.567	0.986	47.06	0.918
Soil with 3%Lime	10	0.1198	0.9276	1630.6	0.9423	5.401	0.768	1498.6	0.942
	20	2.613	0.7632	1345.8	0.9331	0.298	0.951	977.33	0.938
	30	2.7793	0.7737	709.25	0.9366	8.807	0.785	677.98	0.939
	40	0.1294	0.9516	687.02	0.9353	0.298	0.951	492.1	0.939
Soil + 6% Lime	10	0.107	0.933	2329	0.938	2.77	0.792	1703	0.941
	20	0.336	0.924	939.9	0.938	0.775	0.924	780.24	0.941
	30	0.185	0.923	688	0.935	2.658	0.808	539.8	0.939
	40	1.029	0.803	570.9	0.938	2.157	0.808	422.9	0.941
Soil with 1% Cement	10	0.959	0.8	2231	0.935	2.322	0.784	1858.2	0.938
	20	0.351	0.763	1345	0.933	2.326	0.79	1034	0.937
	30	0.307	0.911	874.4	0.939	0.973	0.994	680.4	0.94
	40	0.256	0.919	658	0.938	2.537	0.808	510.577	0.94
Soil with 3% Cement	10	0.117	0.845	2695.8	0.933	0.281	0.834	4338.9	0.979
	20	0.137	0.82	1275	0.93	2.983	0.804	962.63	0.937
	30	2.122	0.821	785.2	0.942	0.461	0.955	1.62E+03	0.942
	40	1.182	0.817	632.57	0.939	0.715	0.986	481.3	0.941
Soil + 10% Fly Ash	10	0.075	0.929	1043.7	0.920	0.174	0.929	927.2	0.932
	20	0.107	0.900	573.4	0.920	1.734	0.793	488.5	0.931
	30	0.091	0.955	415.3	0.919	0.209	0.955	338.8	0.931
	40	0.729	0.865	293.0	0.913	0.069	0.977	246.1	0.928
Soil + 20% Fly Ash	10	0.100	0.908	1385.9	0.911	0.231	0.920	1231.2	0.913
	20	0.143	0.879	761.4	0.911	2.302	0.785	648.6	0.921
	30	0.121	0.933	551.4	0.910	0.278	0.945	449.9	0.921
	40	0.968	0.845	389.1	0.904	0.092	0.967	326.8	0.918
Soil + 30% Fly Ash	10	0.098	0.899	1368.8	0.902	0.228	0.911	1216.0	0.904
	20	0.141	0.870	752.0	0.902	2.274	0.777	640.6	0.912
	30	0.119	0.923	544.6	0.901	0.274	0.936	444.4	0.912
	40	0.956	0.836	384.3	0.895	0.090	0.958	322.8	0.909
Soil + 40% Fly Ash	10	0.109	0.890	1522.8	0.893	0.254	0.901	1352.8	0.895
	20	0.157	0.861	836.6	0.893	2.529	0.769	712.7	0.903
	30	0.133	0.914	605.9	0.892	0.305	0.926	494.3	0.903
	40	1.064	0.828	427.6	0.886	0.101	0.948	359.1	0.900
Soil + 50% Fly Ash	10	0.123	0.948	1711	0.939	0.285	0.948	1520	0.941
	20	0.176	0.918	940	0.939	2.842	0.809	800.8	0.94
	30	0.149	0.974	680.8	0.938	0.343	0.974	555.44	0.94
	40	1.195	0.786	480.4	0.932	0.113	0.997	403.51	0.937

Table 5: Comparative Standard error of estimate (SEE) for soils and amended soils with copper and chromium

Metal	**Composition**	**SEE value for red soil**		**SEE Value for black cotton soil**	
		Pseudo First Order	**Pseudo Second Order**	**PseudoFirst Order**	**Pseudo Second Order**
Copper	Soil	1.178	0.861	14.499	1.023
	Soil + 3 % Lime	4.100	1.002	33.984	1.239
	Soil + 6 % Lime	1.076	1.088	27.464	1.336
	Soil + 1% Cement	7.508	1.190	216.029	1.338
	Soil + 3 % Cement	8.131	1.259	47.890	1.408
	Soil + 10 % FlyAsh	5.564	1.332	32.776	1.774
	Soil + 20 % FlyAsh	10.315	1.457	18.128	1.673
	Soil + 30 % FlyAsh	2.321	1.862	6.451	1.281
	Soil + 40 % FlyAsh	10.315	0.876	156.036	1.761
	Soil + 50 % FlyAsh	3.791	1.003	51.190	1.277
Chromium	Soil	1.310	0.752	13.391	0.925
	Soil + 3 % Lime	129.605	0.922	30.120	1.168
	Soil + 6 % Lime	4.559	1.074	24.642	1.361
	Soil + 1% Cement	213.705	0.867	36.175	1.101
	Soil + 3 % Cement	4.927	0.935	2.482	1.188
	Soil + 10 % FlyAsh	1.665	0.865	5.332	1.235
	Soil + 20 % FlyAsh	4.635	0.976	6.376	1.834
	Soil + 30 % FlyAsh	312.325	1.321	66.125	1.234
	Soil + 40 % FlyAsh	12.325	1.076	16.896	1.135
	Soil + 50 % FlyAsh	4.500	1.190	9.924	1.389

Table 6: Parameters obtained from Elovich Kinetics model with different initial concentrations of copper for different sorbents

Parameters		**Red soil**			**Black cotton soil**		
Sorbent	**Initial Conc mg/l**	**β g/mg**	**α mg/g/min**	**R^2**	**β g/mg**	**α mg/g/min**	**R^2**
Soil	10	58.8	0.98	0.914	76.92	1.99	0.93
	20	166.6	3225.9	0.72	18.87	1.38	0.956
	30	142.86	53.15	0.9	37.04	4.46	0.942
	40	16.13	1.116	0.927	20	4.04	0.927
Soil with 3%Lime	10	52.63	1.45	0.8	52.63	3.09	0.939
	20	23.25	0.91	0.995	47.62	10.27	0.952
	30	14.5	0.814	0.957	47.62	10.27	0.952
	40	9.9	0.62	0.929	14.084	4.3	0.954
Soil + 6% Lime	10	50	0.926	0.922	90.91	8.99	0.922
	20	21.27	0.61	0.959	40	7.68	0.959
	30	13.88	1.043	0.967	26.3	15.93	0.967
	40	9.17	0.616	0.948	17.24	10.74	0.948
Soil with 1% Cement	10	76.9	5.77	0.941	111.11	18.63	0.921
	20	25	0.896	0.936	38.46	1.45	0.926
	30	9.43	0.56	0.978	12.19	2.24	0.981
	40	8	0.72	0.994	11.76	2.955	0.993
Soil with 3% Cement	10	32.25	0.756	0.977	52.63	2.4	0.967
	20	28.57	1.098	0.941	40	5.86	0.953
	30	14.93	0.738	0.964	22.73	4.57	0.964
	40	9.52	1.24	0.972	14.93	5.268	0.981
Soil + 10 % Fly Ash	10	34.736	0.657	0.915	55.650	4.502	0.923
	20	15.715	0.519	0.938	25.502	4.600	0.985
	30	11.999	0.545	0.946	18.566	7.114	0.926
	40	7.333	0.444	0.937	11.129	7.120	0.937
Soil + 20 % Fly Ash	10	37.367	0.809	0.908	64.546	5.545	0.947
	20	16.905	0.639	0.962	29.579	5.666	0.923
	30	12.908	0.671	0.924	21.534	8.761	0.976
	40	7.888	0.547	0.938	12.908	8.769	0.954
Soil + 30 % Fly Ash	10	43.683	0.946	0.899	75.455	6.482	0.938
	20	19.762	0.747	0.952	34.578	6.623	0.914
	30	15.089	0.784	0.915	25.174	10.242	0.966
	40	9.221	0.639	0.929	15.089	10.251	0.944
Soil + 40 % Fly Ash	10	47.367	1.026	0.881	81.819	7.029	0.919
	20	21.429	0.810	0.933	37.494	7.182	0.895
	30	16.362	0.851	0.896	27.297	11.106	0.947
	40	9.999	0.693	0.910	16.362	11.115	0.926
Soil + 50% Fly Ash	10	52.63	1.14	0.972	90.91	7.81	0.972
	20	23.81	0.9	0.993	41.66	7.98	0.993
	30	18.18	0.945	0.991	30.33	12.34	0.991
	40	11.11	0.77	0.985	18.18	12.35	0.98

Table 7: Parameters obtained from Elovich Kinetics model with different initial concentrations of chromium for different sorbents

Parameters		Red soil			Black cotton soil		
Sorbent	**Initial Conc. mg/l**	**β g/mg**	**α mg/g/min**	**R^2**	**β g/mg**	**α mg/g/min**	**R^2**
Soil	10	47.62	0.772	0.942	71.43	1.26	0.925
	20	76.9	5.01	0.897	52.63	4.03	0.941
	30	23.8	1.153	0.893	20.41	2.22	0.983
	40	111.1	1129.2	0.789	13.33	2.12	0.941
Soil with 3%Lime	10	41.66	0.836	0.929	52.63	2.25	0.984
	20	38.46	0.928	0.936	58.82	10.51	0.936
	30	20	0	0.882	62.5	268.3	0.984
	40	21.7	1.355	0.919	33.33	32.44	0.919
Soil + 6% Lime	10	100	3.026	0.925	166.66	84	0.933
	20	25.64	1.257	0.908	37.1	6.46	0.952
	30	18.86	0.778	0.94	34.48	20.67	0.94
	40	16.66	0.98	0.91	24.4	31.1	0.959
Soil with 1% Cement	10	62.5	1.06	0.918	111.1	11.9	0.868
	20	40	0.96	0.943	55.55	6.21	0.943
	30	27.02	1.094	0.91	27.77	1.47	0.982
	40	15.625	0.824	0.923	19.61	4.52	0.939
Soil with 3% Cement	10	76.9	0.915	0.916	90.9	3.78	0.947
	20	41.6	1.02	0.96	62.5	13.66	0.96
	30	22.22	0.96	0.959	33.33	9.34	0.959
	40	19.61	1.195	0.927	29.411	18.75	0.927
Soil + 10 % Fly Ash	10	50.767	2.378	0.915	87.445	37.484	0.923
	20	14.348	0.000	0.938	24.486	8.769	0.985
	30	8.151	0.398	0.946	12.494	2.848	0.926
	40	8.461	0.392	0.937	13.020	5.730	0.937
Soil + 20 % Fly Ash	10	54.613	2.929	0.908	101.424	46.164	0.947
	20	15.435	0.000	0.962	28.400	10.799	0.923
	30	8.769	0.490	0.924	14.491	3.507	0.976
	40	9.102	0.483	0.938	15.102	7.057	0.954
Soil + 30 % Fly Ash	10	63.844	3.424	0.899	118.566	53.967	0.938
	20	18.044	0.000	0.952	33.200	12.624	0.914
	30	10.251	0.573	0.915	16.940	4.100	0.966
	40	10.641	0.564	0.929	17.654	8.250	0.944
Soil + 40 % Fly Ash	10	69.228	3.713	0.881	128.565	58.518	0.919
	20	19.566	0.000	0.933	36.000	13.689	0.895
	30	11.115	0.621	0.896	18.369	4.446	0.947
	40	11.538	0.612	0.910	19.143	8.946	0.926
Soil + 50% Fly Ash	10	76.92	4.125	0.96	142.85	65.02	0.944
	20	21.74	0	0.969	40	15.21	0.964
	30	12.35	0.69	0.95	20.41	4.94	0.95
	40	12.82	0.68	0.947	21.27	9.94	0.947

Table 8: Parameters obtained from Intraparticle diffusion model using different initial concentration of copper with different sorbents

Parameters		**Red soil**			**Black cotton soil**		
Sorbent	**Initial Conc mg/l**	**K_{dif} mg/g/min-$^{0.5}$**	**C mg/g**	**R^2**	**K_{dif} mg/g/min-$^{0.5}$**	**C mg/g**	**R^2**
Soil	10	0.017	0.001	0.914	0.013	0.039	0.93
	20	0.055	0.03	0.911	0.053	0.05	0.956
	30	0.007	0.138	0.9	0.027	0.146	0.942
	40	0.062	0.019	0.927	0.05	0.209	0.927
Soil with 3%Lime	10	0.036	0.019	0.945	0.019	0.085	0.939
	20	0.043	0.013	0.995	0.021	0.189	0.952
	30	0.069	0.038	0.957	0.021	0.189	0.952
	40	0.115	0.149	0.945	0.071	0.274	0.954
Soil + 6% Lime	10	0.02	0.926	0.922	0.011	0.109	0.922
	20	0.047	0.61	0.959	0.025	0.188	0.959
	30	0.072	1.043	0.967	0.038	0.344	0.967
	40	0.109	0.616	0.948	0.058	0.392	0.948
Soil with 1% Cement	10	0.013	0.099	0.941	0.009	0.124	0.921
	20	0.04	0.014	0.936	0.026	0.138	0.926
	30	0.106	0.136	0.978	0.082	0.165	0.981
	40	0.125	0.087	0.994	0.085	0.227	0.993
Soil with 3% Cement	10	0.031	0.03	0.977	0.019	0.066	0.967
	20	0.035	0.011	0.941	0.025	0.163	0.953
	30	0.067	0.055	0.964	0.044	0.209	0.964
	40	0.105	0.051	0.972	0.067	0.301	0.981
Soil + 10 % Fly Ash	10	0.012	0.012	0.915	0.006	0.066	0.923
	20	0.027	0.008	0.938	0.013	0.121	0.985
	30	0.035	0.005	0.946	0.018	0.184	0.926
	40	0.057	0.033	0.937	0.029	0.261	0.937
Soil + 20 % Fly Ash	10	0.013	0.007	0.908	0.008	0.072	0.947
	20	0.030	0.010	0.962	0.017	0.132	0.923
	30	0.039	0.006	0.924	0.023	0.201	0.976
	40	0.064	0.039	0.938	0.039	0.285	0.954
Soil + 30 % Fly Ash	10	0.016	0.008	0.899	0.009	0.085	0.938
	20	0.035	0.012	0.952	0.020	0.154	0.914
	30	0.046	0.007	0.915	0.027	0.235	0.966
	40	0.075	0.046	0.929	0.046	0.333	0.944
Soil + 40 % Fly Ash	10	0.017	0.009	0.881	0.010	0.092	0.919
	20	0.038	0.013	0.933	0.022	0.167	0.895
	30	0.050	0.008	0.896	0.030	0.255	0.947
	40	0.081	0.050	0.910	0.050	0.361	0.926
Soil + 50% Fly Ash	10	0.019	0.01	0.972	0.011	0.102	0.972
	20	0.042	0.014	0.993	0.024	0.186	0.993
	30	0.055	0.009	0.991	0.033	0.283	0.991
	40	0.09	0.055	0.985	0.055	0.401	0.98

Table 9: Parameters obtained from Intraparticle diffusion model using different initial concentration of chromium with different sorbents

Parameters		**Red soil**			**Black cotton soil**		
Sorbent	**Initial Conc mg/l**	**K_{dif} mg/g/min-$^{0.5}$**	**C mg/g**	**R^2**	**K_{dif} mg/g/min-$^{0.5}$**	**C mg/g**	**R^2**
Soil	10	0.021	0.021	0.942	0.017	0.023	0.965
	20	0.02	0.014	0.911	0.019	0.105	0.941
	30	0.038	0.091	0.871	0.049	0.118	0.983
	40	0.031	0.263	0.784	0.075	0.146	0.941
Soil with 3%Lime	10	0.673	0.047	0.9999	0.019	0.061	0.984
	20	0.025	0.027	0.917	0.017	0.163	0.936
	30	0.065	0.039	0.903	0.016	0.37	0.984
	40	0.04	0.132	0.938	0.03	0.366	0.919
Soil + 6% Lime	10	0.01	0.051	0.925	0.006	0.136	0.933
	20	0.039	0.029	0.908	0.027	0.182	0.952
	30	0.053	0.039	0.94	0.029	0.311	0.94
	40	0.06	0.003	0.91	0.041	0.45	0.959
Soil with 1% Cement	10	0.016	0.004	0.918	0.009	0.105	0.868
	20	0.025	0.003	0.947	0.018	0.132	0.943
	30	0.037	0.011	0.91	0.036	0.176	0.982
	40	0.064	0.034	0.923	0.051	0.229	0.939
Soil with 3% Cement	10	0.013	0.005	0.916	0.011	0.066	0.947
	20	0.024	0.022	0.96	0.016	0.173	0.96
	30	0.045	0.005	0.959	0.03	0.235	0.959
	40	0.051	0.0027	0.927	0.034	0.337	0.927
Soil + 10 % Fly Ash	10	0.008	0.012	0.915	0.004	0.094	0.923
	20	0.029	0.000	0.938	0.013	0.163	0.985
	30	0.051	0.045	0.946	0.026	0.153	0.926
	40	0.049	0.046	0.937	0.025	0.215	0.937
Soil + 20 % Fly Ash	10	0.009	0.057	0.908	0.005	0.103	0.947
	20	0.033	0.000	0.962	0.018	0.178	0.923
	30	0.058	0.053	0.924	0.035	0.168	0.976
	40	0.055	0.054	0.938	0.033	0.234	0.954
Soil + 30 % Fly Ash	10	0.011	0.066	0.899	0.006	0.120	0.938
	20	0.038	0.000	0.952	0.021	0.208	0.914
	30	0.067	0.062	0.915	0.041	0.196	0.966
	40	0.065	0.063	0.929	0.039	0.274	0.944
Soil + 40 % Fly Ash	10	0.012	0.072	0.881	0.006	0.131	0.919
	20	0.041	0.000	0.933	0.023	0.226	0.895
	30	0.073	0.068	0.896	0.044	0.212	0.947
	40	0.070	0.068	0.910	0.042	0.297	0.926
Soil + 50% Fly Ash	10	0.013	0.08	0.96	0.007	0.145	0.944
	20	0.046	0	0.969	0.025	0.251	0.964
	30	0.081	0.075	0.95	0.049	0.236	0.95
	40	0.078	0.076	0.947	0.047	0.33	0.947