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Comparative Studies of Sorption of Copper (II) ions from Aqueous Solution Using Synthetic Hematite, Activated Carbon and Composite.

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Abstract

Hematite nanoparticles, activated carbon and composite were used for the removal of copper (II) ions from aqueous solution. The effects of contact time, adsorbent dosage, pH and temperature on the adsorption of Copper (II) ions were studied. The results show that the adsorption of Cu (II) was time, adsorbent dosage, temperature and pH dependent. The thermodynamic studies show that the adsorption process was exothermic in nature. The results obtained show that the uptake of $Cu(II)$ ions onto hematite and activated carbon best fitted the Langmuir isotherm with \mathbb{R}^2 values of 0.9557 and 0.9614 respectively while that of composite best fitted the Freundlich isotherm with \mathbb{R}^2 value of 0.9616. The hematite has the highest adsorption capacity of 21.5 mg Cu(II)/g of adsorbent, activated carbon has higher adsorption capacity of 15.4mg Cu(II) /g of adsorbent while that of composite was 14.6mg Cu(II)/g. Kinetic studies show that pseudo-second-order reaction model best described the adsorption process for all three adsorbents with R^2 value in the range 0.8755-0.9647 indicating a chemisorption process. The thermodynamic results reveal the spontaneity of the reaction for hematite and composite.

Keywords: Nanoparticles, isotherms, composite, synthetic hematite.

1. Introduction.

No doubt, the rapid growth of industrialization worldwide has its own advantages and disadvantages. On the negative side, industrialization has caused day by day contamination of both surface and ground water. For instance, industrial processing of metals and other processes have introduced substantial amounts of potentially toxic heavy metals into the environment. Current treatment of wastewaters does not adequately remove all heavy metals from wastewater and effluents aside from them being very expensive because of the many resources involved. However, efforts have been made to eliminate the heavy metals content by adsorption on various types of adsorbents. Sorbents like activated carbon and

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nanoparticles have been seen as ideal sorbents for heavy metals due to their smaller size and increased surface area (Adegoke and Adekola, 2005, 2012).

Methods used to remove pollutants from wastewater/effluents include: reverse osmosis, chemical precipitation, solvent extraction, ion exchange, adsorption and a few others. However these all have their pitfalls for example, reverse osmosis, though very effective is cost prohibitive as membranes get easily spoiled thereby requiring frequent replacement. Similarly, chemical precipitation is not suitable when pollutants are present in trace amounts and it also produces sludge. Solvent extraction is only considered cost effective only for more concentrated solutions. Ion exchange is more expensive and highly sophisticated. Adsorption remains the only effective, versatile, simple and economical means of treatment of wastewaters/effluents because it can be applied at very low concentration as well as the possibility of regeneration and reuse (Adegoke *et al*., 2013). Not only this, the ability of adsorption to remove toxic chemicals without tampering with the quality of the water or leaving behind any toxic degraded products makes it more preferable to other treatment methods (Rabb *et al*., 2011).

The particle which falls in the size range of 1-100nm, neither quantum nor solid state chemistry can be used satisfactorily to explain the phenomena they exhibit. The particles in this regime are too large to be deemed as molecules but too small to be considered as bulk matter. Thus, they are classified in a different way which lie midway between molecular level system and bulk state. Their relevant chemistry is called "nanoscience" (Leng, 2007).

The application of nanotechnology to the purification and treatment of wastewater/effluents may potentially revolutionize water treatment processes. Due to nanomaterials size which makes them have large surface area, potential for self-assembly, high specificity, high reactivity and catalytic potential makes them an excellent choice for water treatment applications. Nanomaterials are quite an excellent choice of adsorbent and are efficient for the fast adsorption of heavy metal ions and organic molecules from aqueous solution because of their high specific surface areas and absence of internal diffusion resistance.

For the past few years, the focus of many researchers has been on the use of cheap materials as potential adsorbents. Use of agricultural wastes as potential adsorbent has proved to be very effective, cheap and reduced the rate of pollution in the environment. Synthesized nanomaterials have also proved to be effective and their precursors are likewise cheap.

The objectives of this work were to prepare hematite nanoparticles, activated carbon and composite from hematite and activated carbon; to compare the adsorption efficiency and investigate the adsorption characteristics of the each prepared sample in the removal of Cu (II) ions from aqueous solution.

2. Materials and Methods.

2.1 Preparation of Adsorbents

Preparation of Hematite Nanoparticles

Hematite nanoparticles were prepared through the transformation of ferrihydrite method. Five hundred ml (500 ml) of 1M KOH, 50 ml of 1M NaHCO₃ and 40 g of Fe(NO₃)₃.9H₂O in 500 ml deionized water was preheated at 90° C in an oven. Three hundred ml (300 ml) of 1M KOH was added to the ferric nitrate solution (which was reddish brown in colour) giving a dirty brown voluminous precipitate. Then 50 ml of $1M$ NaHCO₃ was added to the brown precipitate mixture. The whole mixture was stirred using a stirrer (STUART model) for 30 minutes. The resulting solution was then aged in oven at 90° C for 48h. After aging, the mixture was allowed to cool and then dialyzed to remove nitrate ions $(NO₃)$. After dialysis, the supernatant was decanted and remaining solution filtered using glass membrane filtration set up. The reddish brown hematite obtained was then dried in oven at 40° C after which it was weighed (Adegoke and Adekola, 2012).

2.2 Preparation of Activated carbon

The activated carbon was obtained from coconut coirpith, an agricultural waste. Activated carbon was prepared from coconut coirpith using chemical activation method (Adegoke and Adekola, 2010). The coirpith was carbonized in muffle furnace at 450° C for 1 hour leaving behind a carbon residue. The carbon residue was then purified using 0.5 M HCl after which it was subjected to chemical activation using $1M H_3PO_4$ (orthophosphoric acid).

Preparation of Composite

The composite was prepared by dispersing activated carbon and hematite in ratio 2:1 in 0.5 M HCl which was vigorously stirred using a stirrer for 1h. The dispersion was then aged for 24h at 80°C. After which the composite material was washed with de-ionized water, filtered and dried in the oven at 100^oC (Kosmulski *et al.*, 2003).

2.3 Characterization of adsorbents

Activated carbon was characterized based on some physical properties such as bulk density, moisture content, loss on mass ignition and pH.

Moisture content was determined by weighing 1.0g of adsorbents into a crucible which was dried in oven at 105° C for 2 hours. It was then removed and cool in a dessicator and weighed. It was reheated at same temperature for 1 hours and allow to cool and weighed. This process was repeated until a constant weight was obtained (Langmuir, 1918).

Bulk density was determined using the Archimedes principle. An empty dried measuring cylinder was weighed and then filled with water and reweighed. It was then dried and filled with each adsorbent and weighed (Toshiguki and Yukata, 2003).

Transmission electron microscopy (TEM) [JEOL TEM 1010 model] and Scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray (EDX) (Carl Zeiss ultra plus field emission electron microscope (FESEM) were used to probe the morphology and elemental composition of the synthesized samples). The crystalline structure of the synthesized hematite and composite were examined using X-ray diffraction (XRD). Fourier transform infrared (FTIR) (SHIMADZU 8400S model) was used to characterize purified activated carbon. Transmission electron microscopy showed the particle sizes of the synthesized material.

2.4 Batch adsorption experiments

Copper (II) chloride (1.058 g) was dissolved in 500 ml of deionized water to give 1000 mg/L of copper (II) solution. Different concentrations of copper (II) solution was then prepared from the stock solution

2.4.1 Effect of Concentration

Different concentrations (0-200 ppm) of aqueous solution of Cu (II) ions were contacted with 0.1g of activated carbon, 50 mg hematite and 50 mg composite. The solution was then agitated at 75 rpm for 2 hours at room temperature $(38^{\circ}C)$. The solution was filtered and the residual copper (II) ions concentration analysed. The equilibrium concentration was determined from the plot of the amount adsorbed against concentrations.

2.4.2 Effect of Contact time

Contact time is a very useful parameter because it determines the adsorption kinetics of the adsorbate (Cu ion) at the equilibrium concentration of 50 mg/L. This effect was investigated by contacting the adsorbents with the copper solution for time intervals of 0-100 minutes. The solution was filtered and the residual copper (II) ions concentration analysed.

2.4.3 Effect of pH

The effect of pH on adsorption was analysed over a pH range 2-10. Twenty millilitre (20 ml) of 50 mg/L copper solution was measured and contacted with 0.1 g, 50 mg and 50 mg of the activated carbon, hematite and composite. The mixture was agitated on a shaker (SHA-B water bath constant temperature oscillator) at 75 rpm for 2 hours. The pH was adjusted using 0.5 M HCl and NaOH. The solution was filtered and the residual copper (II) ions concentration analysed.

2.4.4 Effect of Adsorbent dosage

Different dosages of the adsorbents (0.02-0.50 g) were contacted with 20 ml of 50 mg/L of Copper (II) solution and agitated on a shaker (SHA-B water bath constant temperature oscillator) at 75 rpm for 2 hours at room temperature. The solution was filtered and the residual copper (II) ions concentration analysed.

2.4.5 Effect of Temperature

The effect of temperature (308,328 and 348K) on adsorption of Cu(II) ions on the various adsorbents was investigated by contacting with 0.1 g, 50 mg and 50 mg of the activated carbon, hematite and composite with 20 ml of copper ((II) ions solution. The mixture was agitated on a shaker (SHA-B water bath constant temperature oscillator) at 75 rpm for 2 hours at varied temperature. The solution was filtered and the residual copper (II) ions concentration analysed.

3. Results and Discussions

3.1.0 Characterization of adsorbents

The physical properties of the synthesized adsorbents are shown in the table below:

Table 1: Table showing physical properties of adsorbents used

Nd- Not determined

The SEM micrograph confirms that the synthesized hematite consists of particles which exhibited a spherical-like shape. The SEM micrograph shown in Figures 3.1 and 3.2 for the adsorbents revealed micro-porous structures and heterogenous rough surface.

Fig 3.1a: SEM image of hematite nanoparticle

Fig 3.1b: EDX for hematite nanoparticle

Fig 3.2a: SEM image of Hematite nanoparticles

Fig 3.2b: SEM image of Activated carbon-hematite composite

Fig 3.2c: EDX image of Activated carbon-hematite composite

Fig 3.2d: SEM image of Activated carbon

The TEM micrograph confirms that the synthesized hematite consists of particles with particle sizes in the range 4.61 - 7.85 nm exhibiting a spherical-like shape. The TEM micrograph are shown in figures 3.3 and 3.4.

Fig 3.3: TEM image of Hematite nanoparticle

Fig 3.4: TEM image of Hematite nanoparticle showing particles size in the range 4.61 nm- 7.85nm

 Fig 3.5a: XRD diagram for hematite

 Fig 3.5b: XRD for the composite

Fig 3.5c: XRD of Activated carbon

The intense and sharp peaks obtained from the XRD pattern (Figs 3.5a-3.5b) for hematite and activated carbon indicate that the synthesized adsorbents were highly crystalline which suggests high surface area which definitely will have impact on their adsorption capacity.

Fig 3.5d: FTIR spectrum for activated carbon

The FTIR spectrum for activated carbon displayed the following bands:

3443.05 cm⁻¹: O-H stretching vibrations,

2370.59 cm⁻¹: C≡C stretching vibrations.1618.33cm⁻¹: C=C stretching vibrations,

1396.51cm⁻¹: C-CH₃ deformation,1143.83cm⁻¹, 1047.38 cm⁻¹: C-O-H stretching vibrations

754.19 cm⁻¹: C-H out of plane deformation.

The FTIR spectra obtained were in agreement with the results reported in the study carried out on commercial granular activated carbons. The band in the region of $\approx 1600 \text{ cm}^{-1}$ has been reported for most carbonaceous materials as C=C stretching absorption frequently (Jung *et al.*, 2001). The spectrum in the region of 1200–1000 cm⁻¹ represented C-O stretching vibrations of functional groups such as alcohols, ethers, carboxylic acids and esters.

Upon thermal treatment, activated carbon mixed with $Fe₂O₃$ should decompose on the iron oxide surface to produce elemental carbon, which readily reacts with $Fe³⁺$ to produce reduced species, according to the simplified reactions:

$$
0.5C + 3Fe2O3 \rightarrow 2Fe3O4 + 0.5CO2
$$
\n(1)

$$
0.5C + Fe3O4 \rightarrow 3FeO + 0.5CO2
$$
 (2)

$$
0.5C + FeO \rightarrow Fe + 0.5CO2
$$
 (3)

3.2 Result of Adsorption Studies

3.2.1 Effect of Concentration

The result of effect of concentration on adsorption of copper (II) ions is shown in Fig 3.6a. As the concentration increases, the amount adsorbed increases which shows that there are so many available adsorption sites on the adsorbents used.

Fig 3.6 a: Effect of Concentration on Adsorption of Cu (II) ions

3.2.1 Effect of Contact Time

The result of effect of contact time is shown in Fig 3.6 b. It was observed from the graph that as the time increased, the amount adsorbed also increases for all adsorbent types. Maximum adsorption was observed within 40-100 minutes adsorption for all adsorbents.

Fig 3.6 b: Effect of contact time Adsorption of Cu (II) ions

3.2.2 Effect of pH

It was observed from Fig 3.7 that as the pH increase, the amount adsorbed also increased. Maximum adsorption was observed at pH 6 for hematite and pH 8 for composite sample but for the activated carbon amount adsorbed increases with increasing pH even up to pH 10.

Fig 3.7: Effect of pH Adsorption of Cu (II) ions

From the graphs (Figs 3.6 and 3.7) above, the optimum time and pH for adsorption of Cu (II) ion on hematite was at 100 minutes (percent removal of 99.3%) at pH of 4-5, that of composite was 60 minutes (percent removal of 95.5%) at pH of 6 while that of activated carbon was 80 minutes (84.8%) up to pH of 10.

3.2.3 Effect of Adsorbent Dosage

It was observed that adsorption varied with the different adsorbent dosage ranging from (0.05-0.5)g, this is shown in Figure 3.8. An increase in adsorbent dose results in lowered adsorption. This result reveals that the available sites for adsorption was high for small quantity of each sample. This may be caused by the fact that, with increasing dose, less adsorption sites were available. Also, increase in the mass had little effect on removal efficiency at high adsorbent dose because of the establishment of equilibrium at extremely low adsorbate concentration in solution.

Fig 3.8: Effect of Adsorbent Dosage Adsorption of Cu (II) ions

3.2.4 Effect of Temperature

The effect of temperature (308, 328 and 348K) on adsorption of Cu(II) ions is shown in Fig 3.9. The result showed that as the temperature increases, the amount of adsorbate decreases. It can be deduced that at higher temperatures, the bonds between the adsorbate and adsorbents is being weakened which favours the reverse of adsorption (desorption).

Fig 3.9: Effect of Temperature Adsorption of Cu (II) ions

3.3 Equilibrium Studies

The adsorption capability of adsorbent is a specific function of concentration of adsorbate. The experimental data were modelled using the Langmuir and Freundlich isotherm.

3.3.1 Langmuir Isotherm

The langmuir isotherm fitted the adsorption of Cu(II) on hematite and activated carbon the best with \mathbb{R}^2 values of 0.9557 and 0.9614 respectively. This shows that there is formation of monolayer adsorbate on the surface of hematite and activated carbon. Also the calculated R_L value for hematite and activated carbon was 0.011 and 0.323 respectively $(R_L < 1)$ which shows the adsorption of the adsorbate on hematite and activated caron is favourable. From the graph shown below for composite, using langmuir isotherm to model for the adsorption of Cu(II) on composite isnt the best as it has a low R^2 value of 0.7613 and also its calculated R_L value (0.917) is approximately equal to 1.

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Vermeulan *et al*., 1966). Based upon these assumptions, Langmuir is represented by the following equation:

$$
\frac{c_{\varepsilon}}{Q_{\varepsilon}} = \frac{1}{K q_{max}} + \frac{c_{\varepsilon}}{q_{max}},\tag{4}
$$

where *K* is the Langmuir constant (L·mg⁻¹) related to the apparent energy of adsorption, q_{max} is the quantity of adsorbate required to form a single monolayer per unit mass of adsorbent (mg·g−1), considered as the maximum adsorption capacity and *Q^e* is the amount adsorbed on

unit mass of the adsorbent $(mg·g⁻¹)$ when the equilibrium concentration is C_e $(mg·L⁻¹)$ (Barkat *et al*. 2014).

Figures 4a to 4c show the Langmuir isotherms.

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter RL, which is a dimensionless constant referred to as separation factor or equilibrium parameter.

$$
R_L = \frac{1}{1 + (1 + K_L C_o)},\tag{5}
$$

where C_0 = initial concentration,

 K_L = the constant related to the energy of adsorption (Langmuir Constant).

The R_L value indicates the adsorption nature to be either unfavourable if $R_L>1$), linear if R_L =1, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$ (Guadalupe et al., 2008).

3.3.2 Freundlich Isotherm

From the graph below (Figures 4d - 4e), it can be found that all the three adsorbents used can be modelled with freundlich isotherm with composite being the best fit $(R^2 \text{ value of } 0.9616)$. This suggests that all the three adsorbents have heterogeneous surfaces. The KF value for hematite, activated carbon and the composite are 5.181, 0.388 and 0.344 mg/g. This shows that hematite has the highest adsorption capacity followed by activated carbon with composite having the least adsorption capacity.

This isotherm is commonly used to describe the adsorption characteristics for heterogeneous surface (Hutson and Yang, 1997). These data often fit into the empirical equation proposed by Freundlich:

$$
q_e = K_f C_e^{1/n} \,,\tag{6}
$$

where K_f = Freundlich isotherm constant (mg/g),

 $n =$ adsorption intensity;

 C_e = the equilibrium concentration of adsorbate (mg/L),

 q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing equation (1), we have:

$$
\log q_{\epsilon} = \log K_f + \frac{1}{n} \log C_{\epsilon}.
$$
\n⁽⁷⁾

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process (Voudrias *et al.*, 2002). If $n =$ 1, then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption (Weber and chakravarti, 1974). Also if n lies between one and ten, it indicates a favourable sorption process (Goldberg, 2005).

3.4 Adsorption Kinetics

In order to investigate the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, the pseudo-first order and pseudo-se cond order kinetics was used to test the experimental data of the adsorption of Cu (II) ion on the three adsorbents used. Table 2 shows that the R^2 values for the pseudo-first order were too small, hence it can be said that the experimental data does not fit the pseudo-first order but best fit the pseudosecond order model. This indicates that the rate limiting step is chemisorption that involves valency forces through sharing or exchange of electrons between adsorbent and adsorbate.

The table below shows the parameters of the pseudo-first and pseudo-second orders.Figures 4d to 4f show the kinetics graphs.

	Pseudo-first order parameters					Pseudo-second order parameters		
	qe	qe	K_1	\mathbb{R}^2	qe	K ₂	\mathbb{R}^2	
	(calculated)	(mg/g)	(L/min)		(mg/g)	(g/mg/min)		
			$x10^{-3}$			$\ge 10^{-2}$		
Composite	50.83	36.83	0.9	0.218	17.36	0.08	0.9647	
Hematite	23.17	6.85	4.5	0.109	18.90	0.06	0.9318	
Activated	10.70	5.30	4.1	0.134	6.87	1.42	0.8755	
carbon								

Table 2: Kinetic model constants for the different adsorbents

3.5 Thermodynamic Studies

Table 3 shows that at temperature of 348K, ΔG for the composite was positive which indicates that the process was not spontaneous at this temperature. Also the negative value of ΔH signifies that the adsorption process was exothermic in nature and hence does not require any external heat to drive the adsorption process. The positive value of ΔS for hematite indicates that there is a high degree of disorderliness at the solid/liquid interface.

The spontaneity of a process can be determined by thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS). A spontaneous process will show a decrease in ΔG and ΔH value with increasing temperature. The thermodynamic parameters were calculated based on the following equation:

$$
\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT'},\tag{8}
$$

where K_c (equilibrium constant) = q_e/C_e ,

$$
\Delta G = \Delta H - T \Delta S \tag{9}
$$

Figures 4g to 4i show the thermodynamic graphs:

Fig. 4a: Langmuir isotherm for hematite

Fig. 4b: Langmuir isotherm for AC

Fig. 4c: Langmuir isotherm for composite

Fig. 4d: Freundlich Isotherm for activated carbon

Fig. 4f: Freundlich Isotherm for composite

Fig. 4g: Thermodynamic for AC

Fig. 4h: Thermodynamic for composite

Fig. 4i: Thermodynamic for hematite

Table 3: Showing Thermodynamic parameters for composite and hematite

Table 4: Showing Thermodynamic parameters for activated carbon

4. Conclusion

Three adsorbents (hematite, activated carbon and composite) were prepared, characterized and applied in the sorption of copper (II) ions from aqueous solution. Influence of pH, time, dosage and temperature were investigated. It was observed that as the amount of adsorbents added increases, the adsorption capacity decreases implying a decrease. Adsorption kinetics and thermodynamic studies were also determined on all the three adsorbents. The Langmuir and Freundlich isotherm models were used to described the adsorption data well. Hematite and activated carbon were found to fit the Langmuir isotherm model best. The three adsorbents were found to follow the pseudo-second order model .

Also comparing their adsorption capacity it can be observed that hematite proved to be the best adsorbent for the removal of copper (II) ions followed by activated carbon then the composite have the least adsorption capacity. From the thermodynamic studies carried out, it was found that the adsorption process was exothermic in nature and hence require no external heat. This explains the reason why amount adsorbed decreases with increase in temperature. The adsorption process of hematite has a high degree of disorderliness while that of activated carbon and composite were found to be low. From this, it can be concluded that hematite, activated carbon and its composite can be used for removal of Cu(II) ions from industrial effluets or wastewaters.

References

- Adegoke, H. I. and Adekola, F. A. (2010): Removal of phenol from aqueous solution by activated carbon prepared from some agricultural materials, *Advances in Natural and Applied Sciences*. **4**(3), 293-298.
- Adegoke, H. I. and Adekola, F. A. (2012): Equilibrium Sorption of Hexavalent chromium from aqueous solution using synthetic hematite. *Colloid Journal.* **74**(4), 420-426.
- Adegoke, H. I., Adekola, F. A., Fatoki, O. S. and Ximba B. J. (2013): Sorptive Interaction of Oxyanions with iron oxides: A review. Polish Journal Environmental Studies **22**(1), 7-24.
- Barkat, M., Chegrouche, S., Mellah, A., Bensmain, B., Nibou, D. and Boufatit, M., (2014), Application of Algerian Bentonite in the Removal of Cadmium (II) and Chromium (VI) from Aqueous Solutions. *Journal of Surface Engineered Materials and Advanced Technology*. **4**, 210 – 226.
- De la Rosa, G., Reynel-Avila, H. E., Petriciolet, A. B., Cano-Rodríguez, I. C., Velasco-
- Santos, I. and Martínez-Hernández, A. L. (2008): Recycling poultry feathers for Pb removal from wastewater: kinetic and equilibrium studies. *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*. **2** (11), 338-346.
- Goldberg, S. (2005): *Equations and Models Describing Adsorption Processes in Soils: Chemical Processes in Soils*, SSSA Book Series (8).
- Guadalupe, R., Reynel-Avila, H. E., Petriciolet, A. B., Cano-Rodríguez, I. C., Velasco-Santos, I. and Martínez-Hernández, A. L. (2008): Recycling poultry feathers for Pb removal from wastewater: kinetic and equilibrium studies. *Proceedings of World*

Academy of Science, Engineering and Technology. **30**.

- Langmuir, I. (1918): The adsorption of gases on plane surfaces of glass, mica and platinum, Journal American Chemical Society **40**, 1362-1403.
- Hall, K. R., Eagleton, L.C., Acrivos, A. and Vermeulen, T. (1966): Pore and solid-diffusion kinetics in fixed bed adsorption under constant-pattern conditions. *Industrial and Engineering Chemistry Fundamentals*. **5** (2), 212–223.
- Hutson, N. D. andYang, R. T. (1997): Theoretical basis for the Dubinin Radushkevich (DR) adsorption isotherm equation. *Adsorption*. **3** (3), 189-195.
- Jung, M., Ahn, K., Lee, Y., Kim, K., Rhee, J., Park, T. and Paeng, K. (2001): Adsorption characteristics of phenol and chlorophenols on granular activated carbon (GAC), *Microchemical Journal.* **70**, 123-131.
- Kosmulski, M., Macka, E., Jartych, E., Rosenholm, J. B. (2003): Synthesis and characterization of goethite and goethite-hematite composite: Experimental Study and Literature Survey. *Advanced Colloid and Interface Sciences.* **103**, 57-76.
- Leng, T. W. (2007): Synthesis and characterization of magnetite and magnetite-epoxy polymers nanocomposites and their thermal and electrical behaviour. M.Sc thesis. Submitted to University of Science, Malaysia. 143pp.
- Rabb, C., Simko, M., Gazo, A., Fiedeler, U. and Nentwich, M. (2011): What are synthetic nanoparticles, *Nano trust dossiers*. **002en,** 1-3.
- Toshiguki, S. and Yukata, K. (2003): Pyrolysis of plant, animal and human wastes: Physical and chemical characterization of the pyrolytic product. *Bioresource technology*. **90**(3), 241-247.
- Vermeulan, T. H., Vermeulan, K. R., and Hall, L.C. (1966): Fundamental*. Industrial Engineering Chemistry.* **5**, 212–223.
- Voudrias, E., Fytianos, F. and Bozani, E. (2002): Sorption Description isotherms of Dyes from aqueous solutions and Wastewaters with different Sorbent materials. *The International Journal.* **4**(1), 75-83.
- Webber, T. N. and Chakravarti, R. K. (1974): Pore and Solid Diffusion Models for fixed bed Adsorbers. *Journal of American Institute of Chemical Engineers*. **20**, 228-238.