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KINETIC AND EQUILIBRIUM STUDIES OF WASTE POLYETHYLENEDOPED NANO-COMPOSITE FOR DYESTUFFS REMOVAL

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ABSTRACT: *A series of studies have been conducted on the removal of the basic, and acid dyestuffs malachite green and acid red 8 using polyethylene/ monomrillonite/ nano-composite. Waste polyethylene was collected from green house as an adsorbent. The batch adsorption experiments were conducted under various operating parameters like initial dye concentration, adsorbent dose, pH and temperature. The equilibrium data fitted well to the Freundlich isotherm equation. The adsorption efficiency, adsorption energy, adsorption capacity, intensity of adsorption is calculated. The experimental data fitted very well with second order kinetic model suggesting chemisorption. Significant effect on adsorption was observed on varying the pH. Thermodynamic parameters such as ΔH, ΔS, and ΔG were evaluated. The positive ΔH value and pH dependent results suggest that the adsorption dyes involves physisorption mechanism.*

KEYWORDS: Kinetic and Equilibrium Studies, Waste Polyethylenedoped Nano, Composite for Dyestuffs Removal

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INTRODUCTION

Dyestuffs are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora and increases the organic loads (1).Dye-containing wastewater is a matter of concern for both toxicological and esthetical reasons, and the removal of dyes from wastewater has received considerable attention over the past decades [2,3]. Various techniques, including coagulation, chemical oxidation, membrane separation, electrochemical process and adsorption techniques have been evaluated to decrease the dyes discharge into the water bodies [4-6]. In addition of easy access, adsorption is an effective method as the dissolved dye compounds attach themselves to the surface of adsorbents easily [7-10]. Due to the versatility and the high adsorption capacity,activated carbon is a widely used adsorbent with great success in wastewater treatment [11-14]. However, there have some concerns of using activated carbon for the adsorption of dyes, such as higher operating cost, difficulty separation, problems of regeneration, which are limits its commercial application.
Nowadays, many researchers have focused on the alternative low-price adsorbents such as clays [15,16]. The wide usefulness of clay is a result of its high specific surface area, its physico -chemical properties, and its typical structural properties [17-20]. Montmorillonite is an interstratified layered silicate mineral consisting of a regular (2:1) stacking. The cations of Na^+, K^+ and Ca^{2+} lie in the interlayer region between 2:1 Montmorillonite -like layers, while the exchangeable hydrated cations reside in the latter. Its structure has provided Montmorillonite with good adsorption properties [21]. The physico-chemical behavior rectories are governed

by the extent and the nature of their external surface, which can be modified by suitable acid or thermal 40 treatments [22].
The present study aims to evaluate the efficiency of waste polyethylene doped nano-composite for the removal of acid and basic dyestuffs from aqueous solutions.

MATERIALS AND METHODS

Materials

The materials used for the preparation of polypropylene/ montmorillonite nano-composites are:

1. Waste polyethylene sheets from greenhouse;
2. Acid dyestuff, namely, Acid Red 8 (Aldrich);
3. Basic dyestuff, namely, malachite green was supplied by Bayer AG (Leverkusen, Germany).
4. Hydrochloric Acid and sodium hydroxide were provided from Merck – Darmstadt – Germany.
5. Montmorillonite clay (MMT) with cation exchange capacity (CEC) 100 meq per 100g was supplied by Süd-Chemie – Moosburg –Germany.

Chemicals and Reagents

Montmorillonite (MMT)

Montmorillonite is a raw material which is used in the preparation of polymer/ clay nanocomposites where Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals (Figure 1) [23]. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has two tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately 1 micrometer. Montmorillonite water content is variable and it increases considerably in volume when it absorbs water [24]. Chemically, it is hydrated sodium calcium aluminum magnesium silicate hydroxide $(Na, Ca)_{0.33}(Al, Mg)_2(Si_4O_{10}) (OH)_2 \cdot nH_2O$. Potassium, iron, and other cations are common substitutes; the exact ratio of cations varies with source. The montmorillonite minerals occur in very small micron size less than 2 µm. They are fine-grained and thin-layered. The building blocks model structure of MMT, proposed by Hoffmann, Endell and Wilm consists of two fused silicon-oxygen tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminium or magnesium hydroxide. Excess of negative charges within the montmorillonite layers is due to isomorphous substitution of Si^{4+} for Al^{3+} in the tetrahedral and of Al^{3+} for Mg^{2+} in the octahedral sheet [85]. These negative charges are counterbalanced by cations such as Ca^{2+} and Na^+ situated between the layers. These cations between the layers are part of the cation exchange capacity (CEC) of clay. Montmorillonite has a particularly large surface area when it is dispersed in water; one gram of MMT has a surface area of up to 800 square meters. The clay layers are held together by weak bonding between the oxygen in the tetrahedral and the charge-balancing cations and they can be easily separated. The gallery space between clay layers depends on the type of cations (monovalent cations like Na^+ lead to more expansion than divalent cations like Ca^{2+}) and the concentration of ions. The sum of the single layer thickness and the interlayer represents the repeat unit of the multilayer material, so called d-spacing or basal spacing, and is calculated from the (001) harmonics obtained from X-ray diffraction patterns.

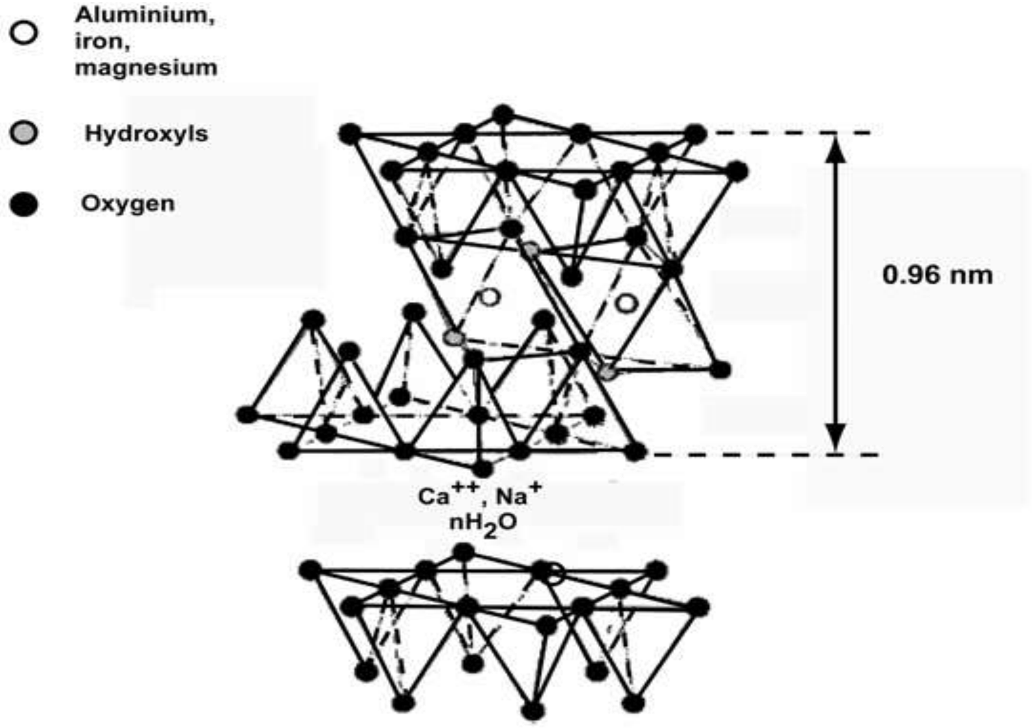

Figure (1): Structure of 2:1 phyllosilicates

The physical dimensions of MMT give it unique properties as a filler material. The basic 2:1 sheet structure results in high aspect ratio sheets with a thickness of 1 nm and lengths of up to 300 nm. A consequence of this high aspect ratio is that small amounts of silicate have very large surface areas. The presence of a large surface area for interaction is a valuable characteristic in fillers. The tremendous surface area available for polymer-clay interaction allows polymer chains to effectively transfer stress into filler particles [25]. In addition, high aspect ratio particles can be used to improve the barrier properties of polymer membranes by increasing the tortuosity of the material [26].

Preparation of Polyethylene/ Montmorillonite Nano-composite by Direct Melt Spinning Intercalation Method

Polymer melt-direct intercalation is an approach to make polyethylene/montmo- rillonite nano-composites using a conventional polymer extrusion process. Polyethylene was melt and mixed with the clay (1-3% Wt) using one liter reactor.

The rotational speed 400 rpm for 6 hours in order to have high shear stress and the temperatures of the reactor reached to 250 ^{o}C.

Analytical Measurements

1-The UV Spectra of the adsorbent were recorded at UV-vis. Spectophotometer (Perkin – Elmer), equipped with a quartz cell having a path length of 1 cm at λ_{max} =520 nm .

2- **Scanning Electron Microscope (SEM):**

SEM analysis using zeiss , DSM 962 microscope .

Adsorption experiments

The effect of pH on the amount of the acid dye removal was analyzed over the pH range from 2 to 6, which were adjusted by 0.6 mol/L HCl solution. A 20 mL of the dye solutions (20 mg/L) and 0.1 g adsorbent was mixed in a flask. The flasks were agitated for 120 min in a constant temperature oscillator operated at 150 rpm. The temperature was controlled at 298 ^{o}K. The residual concentration of the dye in the solution was analyzed and measured using Perkin Elmer UV-Vis Spectrophotometer at its maximum absorption wavelength (520 nm). For the kinetic studies, 0.3 gram of the adsorbent was added to 50 ml dye solution.The initial concentrations of the dye solutions were 50, 100, 150 and 200 mg/l, and the experiments were carried out at 25, 35, 40 and 45^{o}C, respectively. The treated samples were then collected and centrifuged at different time intervals. The remaining concentrations of the dye in the solutions after adsorption were analyzed and measured as before.Freundlich isotherms were used to analyze the equilibrium adsorption data. The data obtained in batch mode studies were used to calculate the equilibrium dye adsorption quantities. It was calculated for adsorptive quantity of the dye by using the following expressions [27]:

$$\% \text{ Removal} = (C_0 - Ce) / C_0 \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$Q_e = (Co - Ce) / ms \times 100\% \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where C_0 in mg/L, is representing the initial concentration of dye solution, and, Ce in mg/L represents the equilibrium concentration of dye in the aqueous solution, while, ms in g/L is the adsorbent dose and qe in mg/g is the amount of the adsorbed dye onto the adsorbent which gives the equilibrium absorption.

RESULT AND DISCUSSION

1-Characterization of solids

Scanning electron micrographs of the surface morphology of the samples under investigations are given in Figs 2-a & 2-b. The figures show the differences in the surfaces

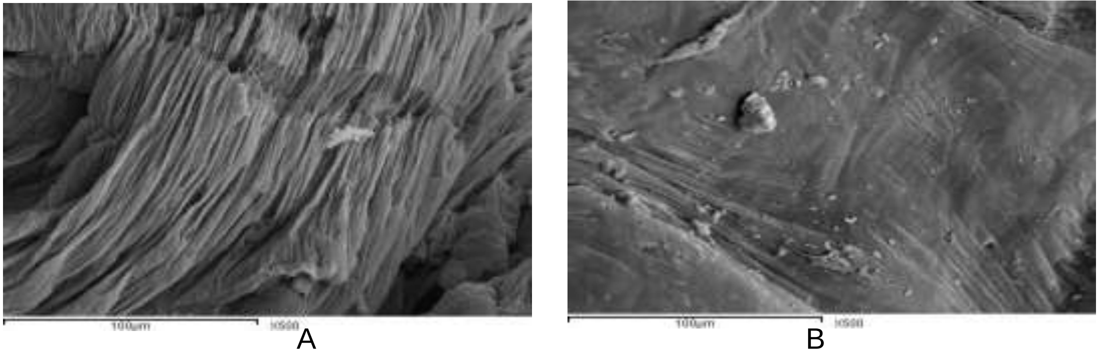
A B

Fig.2-a : SEM of A) Pure P.E. and B) P.E – MMT matrix under magnification (X=500).

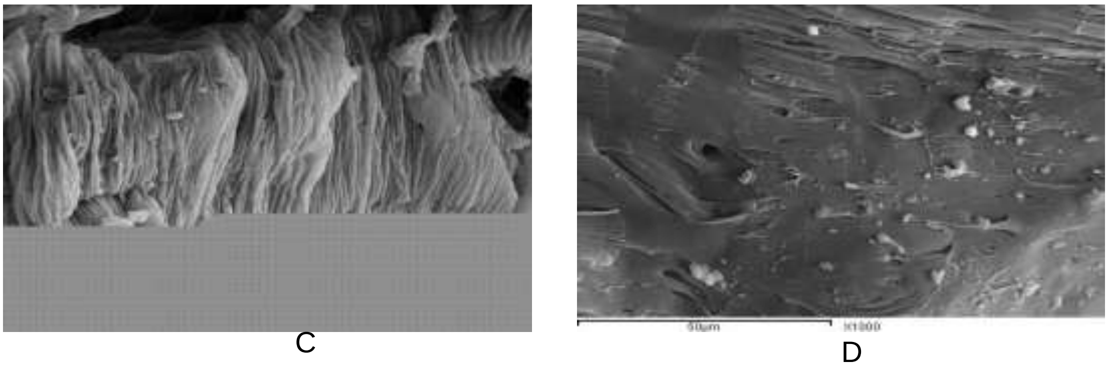
C D

Fig.2-b : SEM of C) Pure P.E. and D) P.E – MMT matrix under magnification (X=1000).

The samples revealed well-developed parallel pore chanels (100µm), the addition of MMT, well dispersed on the intra-surface forming cavities and cracks on the external surface. Also, we observe a very developed porosity on the surface with certain homoginity.

Dye type and pH effect :

It is known that the solution pH can affect the surface charge of the adsorbent, the degree of ionization of the different pollutants, the dissociation of functional groups on the active sites of the adsorbent as well as the structure of the dye molecule [28]. The solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent. So the solution pH is an important parameter during the dye adsorption process.

At pH 2-6, time 120 min, T 25°C & 150 rpm, PE dose 10 g/L, Dye conc. 50 mg/L, 1%, Clay & 0.1M NaCl

pH-value	Dye removal %	
	Pure PE + dye	PE + clay + dye
Acidic dye at pH 5	47	81
Basic dye at pH 10	34	27

When acid dye is used and pH decreased, H^+ ions concentration increased in the adsorption medium which is favored for the negatively charged nano surface.

On the other hand, when basic dye is used, a remarkable reduction was detected due to an increase in repulsion reaction between negative dye as well as nano surface components.

For acid dye:

At present study, the effect of pH on the acid dye adsorption capacities of pure PE and PE + clay were conducted at varying pH (pH 2: 6) with 50 mg / l fixed initial dye concentration and adsorbent dosage 10 g / l for 120 min. It can be seen from Fig (**3**) that the adsorption of acid dye onto PE and PE+ clay is intimately dependent on the pH of solution. The adsorption capacity of dye increases with increasing solution pH from 2 to 6. The maximum adsorption capacity of the PE+ clay was 86 % of the dye removed at pH from 2 to 3 [29,30] .

pH-values	**Dye removal %**	**Equilibrium Abs.**
2	**86**	**4.3**
3	**86**	**4.3**
4	**85**	**4.35**
5	**81**	**4.56**
6	**79**	**4.58**

3- Dye concentration:

At pH 2, time 120 min, Temp 25 °C, 150 rpm, Adsorption dose 10 g/l, Dye conc. (50 -200) mg/l, Nano-clay 1%, NaCl 0.1 M

Initial dye conc. (mg/L)	**Dye removal %**	**Equilibrium Abs.**
50	86	4.3
100	81	4.5
150	64	5.7
200	49	7.5

The initial dye concentrations provide an important driving force to overcome the mass transfere resistance of the dye between the aqeous phases and the solid phases (31).
The adsorption of dye on adsorbent was studied by varying the concentration of initial dye from 50 to 200 mg L^{-1}. It was observed that as initial dye concentration increased, the % of dye removal decreased, consequently the % adsorption increased (Fig 4). Moreover, the equilibrium absorption (qe) increased due to the increasing of the dye adsorbing ions available for the binding sites in the nano surface also due to the increased surface area and availability of more adsorption sites (32,33).

Adsorbent dose:
The adsorbent concentration is an important parameter because this determines the capacity of the adsorbent for a given initial dye concentration. In order to attain the optimal amount of adsorbent for the adsorption of dye, the experimental conditions were:
pH 2, Time 120 min, Temp 25 ^{o}C, 150 rpm, Adsorption dose (1 -15) g/l, Dye conc. 50 mg/l, Nano 1%, NaCl 0.1M

Adsorbent dose (g/L)	Dye removal %	Equilibrium Abs.
1	15	24.6
3	43	8.6
5	67	5.5
10	86	4.3
15	86	4.3

Dye removal increased with increasing the adsorption dose due to the increasing of adsorption surfaces area.
As it can be seen from Fig. (5), the adsorption percentage increased with the increasing amount of adsorbent, and when the amount becomes 10 mg, the adsorption percentage reached 86%. An increase in the adsorption rate with adsorbent dosage can be attributed to increase surface area and the availability of more adsorption sites (34).

Temperature:
pH 2, time 120 min, Temperature (25- 40) ^{o}C, 150 rpm, Adsorption dose 10 g/l, Dye conc. 50 mg/l, Nano 1%, NaCl 0.1M

Temperature	Dye removal %	Equilibrium Abs.
25	86	4.3
30	89	4.15
35	90	4.1
40	90	4.1

Dye removal increased with increasing the temperature due to the increasing of the clay surface penetration rate at high temperature as indicated in Fig (6).

Ionic salt addition:

pH 2, time 120 min, Temp 25 °C, 150 rpm, Ads. dose 10 g/l, Dye conc. 50 mg/l, Nano 1%, NaCl (0.01- 0.2) M

Ionic salt conc.	Dye removal %	Equilibrium Abs.
-----	72	5.13
0.01	77	4.80
0.05	81	4.56
0.10	86	4.30
0.15	86	4.30
0.20	86	4.30

Dye removal increased with increasing the concentration of ionic salt addition which could be attributed to increasing of intermolecular forces as Vander Valls .

The effect of sodium chloride on the adsorption of acid dye on PE + clay is shown in Figure (7). In a low solution concentration of NaCl had little influence on the adsorption capacity. At higher ionic strength, the adsorption of acid dye will be increased due to partial neutralization of positive charge on the surface and consequent compression of the electrical double layer by the chloride anion. The chloride ion can also enhances adsorption of **acid dye** on **PE + clay** by pairing of their changes and hence reducing the repulsion between the **dye** molecules adsorbed on the surface (35).

Effect of Nano Clay Percentage:

The percentage of nano-clay varied from 1.0 to 3.0% , has been studied at the corresponding values of pH 2, time 120 min, Temp 25 °C, 150 rpm, Adsorption dose 10 g/l, Dye conc. 50 mg/l, and NaCl 0.01M)

Nano Clay %	Dye removal %	Equilibrium Abs.
1.0	86	4.30
1.5	92	4.00
2.0	95	3.89
3.0	95	3.89

Dye removal increased with increasing the clay percentage till 2%, then the removal was constant because the clay layers become closed for more dye penetration as shown in Fig (8).

Adsorption Isotherm Isotherm study can describe how an adsorbate interacts with adsorbent. The isotherm provides a relationship between the concentration of dye in solution and the amount of dye adsorbed on the solid phase when both phases are in equilibrium. The experimental data were analyzed according to the Freundlich equation The Freundlich isotherm was represented by

$$\log Q_e = \log K_f + 1/n \log C_e$$

Where Q_e is the amount of acid dye adsorbed (mg g^{-1}),C_e is the equilibrium concentration of dye in solution (mg L^{-1}) and n is constant greater than unity, 1/n is the intensity of adsorption and K_f measures the adsorbent capacity. Figs (9,10) represent linear plots of $\log Q_e$ versus log C_e, it shows that the adsorption of dye obeys the Freundlich adsorption isotherm. The values of K_F and n given in these figures indicate that there is an increase in negative charges on the adsorbent surface that makes electrostatic force like Van der Waals between the catalyst surface and dye. The molecular weight, size and radii either limit the possibility of the adsorption of the dye on the adsorbent. The values clearly show the adsorption capacity. The intensity of adsorption is an indicative of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physi-sorption[36,37]. However, the multilayer adsorption of dye through the process may be possible. The values of n, indicating the adsorption is much more favorable (38). The Freundlich constant, K_F, can be expressed in term of a dimensionless constant, separationfactor (S_F), which is defined

$$\mathbf{S_F = 1/\ 1+K_f\ C_o}$$

Where $K_F$is the Freundlichconstant and C_o(mg/l) is the initial concentration of the adsorbate. The smaller S_F value indicates a highly favorable adsorption (39).

Effect of temperature

The adsorption capacity K_f increased with increase in the temperature of the system from 25-40 °C . Thermodynamic parameters such as change in free energy ($\Delta G°$, JK^{-1} mol^{-1}) , enthalpy ($\Delta H°$, kJ mol^{-1}) were determined using the following equations:

$$K_o \quad = C_{solid} / C_{liquid}$$

$$\Delta G° = - RT \ln K_o$$

$$\text{Log } K_o = \Delta S° /(2.303RT) - \Delta H° / (2.303 RT)$$

Where K_o is the equlibrium constant, C_{solid} is the solid phase concentration at equlibrium (mg L^{-1}) , C_{liquid} is the liquid phase concentraion at equlibrium (mg L^{-1}) , T is the temperature in Kelvin and R is the gas constant . The $\Delta H°$ and $\Delta S°$ values obtained from the slop and intercept of Van,t Hoff plots have presented in Table 1 . The value of $\Delta H°$ =26.7kJ mol^{-1} indicates the physisorption . From the results we could make out that physisorption is much more favourable for the adsorption of dyestuffs. The positive value of $\Delta H°$ shows the endothermic nature of adsorption and it governs the possibility of physical adsorption (37,40). Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, these rules out the possibility of chemisorption (40,41). The low $\Delta H°$ value depicts dye is physisorbed onto adsorbent. The positive values of $\Delta G°$ (Table 1), shows that the adsorption is highly favourable and spontaneous, while $\Delta S°$ shows the increased disorder and randomness at the solid solution interface with adsobent (40-42) .

CONCLUSION

The present study shows that the use of waste PE as adsorbent for acid as well as basic dyestuffs doesn't fulfill any detectable adsorption, while addition of MMT to waste PE can be used as an effective adsorbent for the removal of acid dye.The experimental data were very well corelated by Freundlich adsorption isotherm and its parameters were reported. The amount of acid dye adsorbed increased with decreasing of: pH values; initial dye concentration; and addition of low concentration from NaCl as ionic salt, while it increased with adsorbent dose and reaction temperature. The values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ show that the (PE + MMT) employed has a considerable potential as an adsobent for the removal of acid dyestuffs.

REFERENCES

1- B.Paul, K.P.Rawat , K.S.S. Sarma, and Sabharwal , " Decoloration and degradation of Reactive Red -120 dye by electron beam irradiation in aqueous solution ", Applied Radiation and Isotopes, vol. 69, no.7, pp. 982-987, 2011.
2-Gupta, V. K. J Environ Manage 2009, 90, 2313.
3- Rafatullah, M.; Sulaiman, O.; Hashim, R.; Ahmad, A. J Hazard Mater 2010, 177, 70.
4- Shen, D. Z.; Fan, J. X.; Zhou, W. Z.; Gao, B. Y.; Yue, Q. Y.; Kang, Q. J Hazard Mater 2009, 172, 99.
5- Weng, C. H.; Pan, Y. F. J Hazard Mater 2007, 144, 355.
6- Almeida, C. A. P.; Debacher, N. A.; Downs, A. J.; Cottet, L.; Mello, C. A. D. J Colloid Inter Sci 2009, 332, 46.
7- Liu, Q. S.; Wang, T. Z.; Jiang, J. P.; Li, N. ChemEng J 2010, 157, 348.
8- Li, Q.; Yue, Q. Y.; Su, Y.; Gao, B. Y.; Sun, H. J. ChemEng J 2010, 158, 489.
9- Hong, H. L.; Jiang, W. T.; Zhang, X. L.; Tie, L. Y.; Li, Z. H. Appl Clay Sci 2008, 42, 292.
10- Macedo, J. S.; Costa Júnior, N. B. J Colloid Inter Sci 2006, 298, 515.
11- Yanagisawa, H.; Matsumoto, Y.; Machida, M. Appl Surf Sci 2010, 256, 1619.
12- Santhi, T.; Manonmani, S.; Smitha, T. International J EngSciTechnol 2010, 3, 287.
13- Ahmed, E. N.; Ola, A.; Amany, E. S.; Azza, K. J Hazard Mater 2009, 161, 102.
14- Huang, C. C.; Chen, H. M.; Chen, C. Hung. Int J Hydrogen Energy 2010, 35, 2777.
15- Ijagbemi, C. O.; Baek, M. H.; Kim, D. S. J Hazard Mater 2010, 174, 746.
16- Huang, Y.; Ma, X. Y.; Liang, G. Z.; Yan, Y. X.; Wang, S.H. ChemEng J 2008, 138, 187.
17- Gan, F. Q.; Zhou, J. M.; Wang, H. Y.; Du, C. W.; Chen, X.Q. Water Res 2009, 43, 2907.
18- Mohammad, A.; Majeda, A. G.; Khraisheh, A. M.; Mohammad, N. M.; Ahma, S. A. J Hazard Mater 2009, 165, 589.
19- Balci, S. Clay Miner 1999, 34, 647.
20- Gonzalez, F.; Pesquera, C.; Blanco, C.; Benito, J.; Mendioroz, S.; Pajares, J. A. Appl Clay Sci 1990, 5, 23.
21- Gonzalez-Pradas, E.; Villafranca-S anchez, E.; Villafranca-S anchez, M.; Del Rey-Bueno, F.; Valverde-Garc, A.; Garcıa-Rodrguez, A. J ChemTechnol Biotechnol 1991, 52, 211.
22- Olivier, J. P.; Occelli, M. L. MicroporMesopor Mater 2003, 57, 291.
23- S.S. Ray , M. okamoto , prog . polym . S G : , 28(2003) 1539 .
24- J . Lusis , R . T . Woodhams , M . Xanthos , polym . Eng . SG : 13 (1973) 139 .
25- H . Shi , T . Lan , T . J . Pinnavaia , Chem . Mater . 8 (1996) 1584 .
26 P . B . Messersmith , E .P . Giannelis , J . polym . SG : part A : polym . chem. 33 (1995) 1047 .
27- Edris Bazrafshan et al, J. of Chem. Volume 2013 (2013) ID 938374 .
28- L. Ai, C. Zhang , F. Liao et al., " Removal of methylene blue from aqueous solution with magnetite loaded multi – wall carbon nanotube : kinetic , isotherm and mechanism analysis", Journal of Hazardous Materials, vol . 198, pp . 282 -290, 2011 .

29- M. Shirmardi , A.R. Mesdghinia , A. H. Mahvi, S. Nasseri, and R. Nabizadeh, “Kinetics and equilibrium studies on adsorption of acid red 18 (Azo – Dye) using multiwall carbon nanotubes (MWCNs) from aqueous solution, “ E- Journal of Chemistry , vol. 9, no.4, pp.2371-2383, 2012 .

30- G.Absalan, M.Asadi, S. Kamran, L. Sheikhian, and D. M. Goltz, “ removal of reactive red-120 and 4-(2-pyridylazo) resorcinol from aqueous samples by Fe_3O_4 magnetic nanoparticles using ionic liquid as modifier ,”journal of Hazardous materials, vol. 192, no.2 , pp.476 -484 , 2011 .

31- M. Anbia and S.A. Hariri, “ Removal of methylene blue from aqueous solution using nanoporous SBA- 3, Desalination” , vol. 261, no. 1-2, pp. 61-66, 2010.

32- ISI, Activated Carbon , Powdered and Granular- Methods of Sampling and Tests, 2nd Revision, First Print, Bureau of Indian Standards, IS 877: -FEB 1992.

33- Jafar Ahmed ,A; Balakrishnan ,V. J. Chem. Pharm. Res., 2010 ,2 (3), 733.

34- R.K. Rajoriya , B. Parasad , I.M. Mishra, and K. L. Wasewar , “Adsorption of benzaldehyde on granular activated carbon : Kinetics, equilibrium, and thermodynamic, “ Journal of Hazardous Materials, vol. 196, pp. 109 – 114 ,2011.

35- Jafar Ahmed , A.; Suganthana , B .J. Ind. Chem . Soc ., august 2006, 83, 792 – 795,

36- Langmuir , I. J . Am. Chem. Soc ., 1918 ,40 , 1361.

37 – Freundlich , H . Phy .Chemie ., 1906 , 57 , 384 .

38- Krishna , D. G.; Bhattacharyya , G . Appl. Clay Sci ., 2002, 20, 295 .

39- PanidaSampranpiboon , and PisitCharnkeitkong , International Journal of Energy and Environment , Issue 3 , Volume 4, 2010, 98.

40- Balasubramanian, N.; Jafar Ahhmed, A, J. Ind. Coun. Chem, 2003, 20(2(, 7-12.

41- Karunakaran, K.; Thamilarasu, P. Arch. App. Sci. Res., 2010, 2(1), 176.

42- Krishna, D. G.; Bhattacharyya, G. Appl. Clay Sci., 2002, 20, 295.

Fig (3) Effect of pH value on the absorption of acid dye using different samples

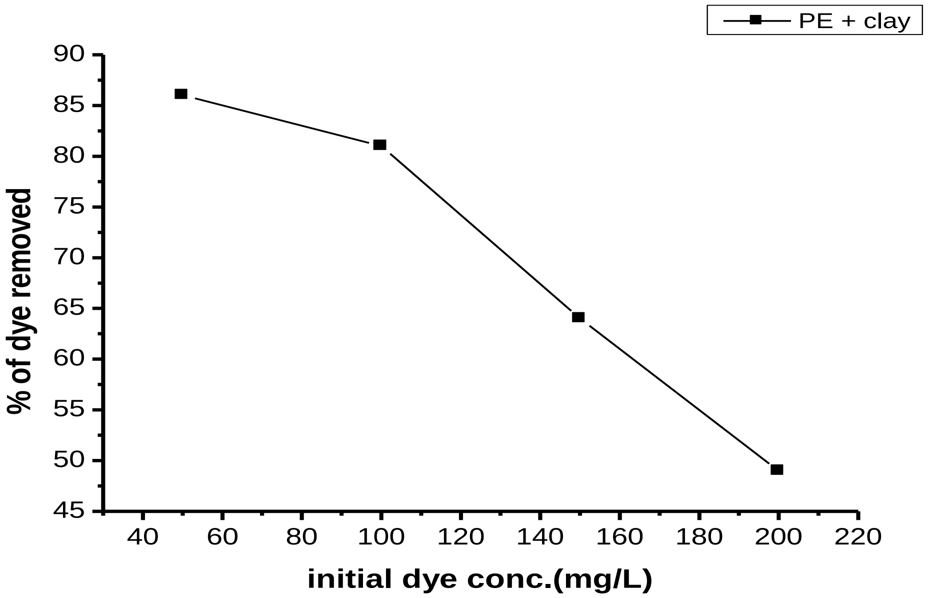

Figure (4) Effect of initial acid dye concentration on the dye adsorption rate on PE at adsorbent dose 10 g/l , pH 2, contact time 120 min, & temp 25ºC .

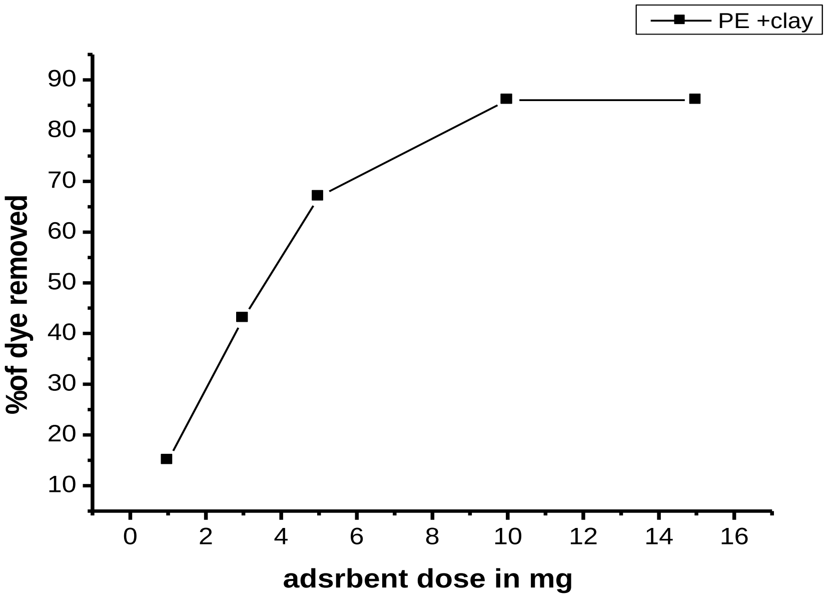

Figure (5) Effect of adsorbent dose on the adsorption of acid dye by PE, at dye conc. 50 mg/l, pH 2, contact time 120 min, & temp 120 ºC .

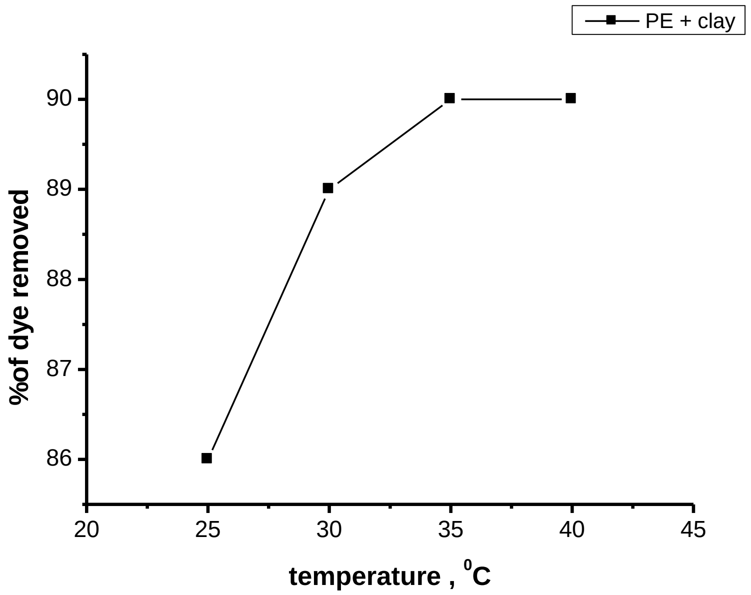

Figure (6) Effect of temperature on the dye adsorption rate on PE at adsorbent weight 10 g/l , pH 2, contact time 120 min, & dye conc. 50 mg/l.

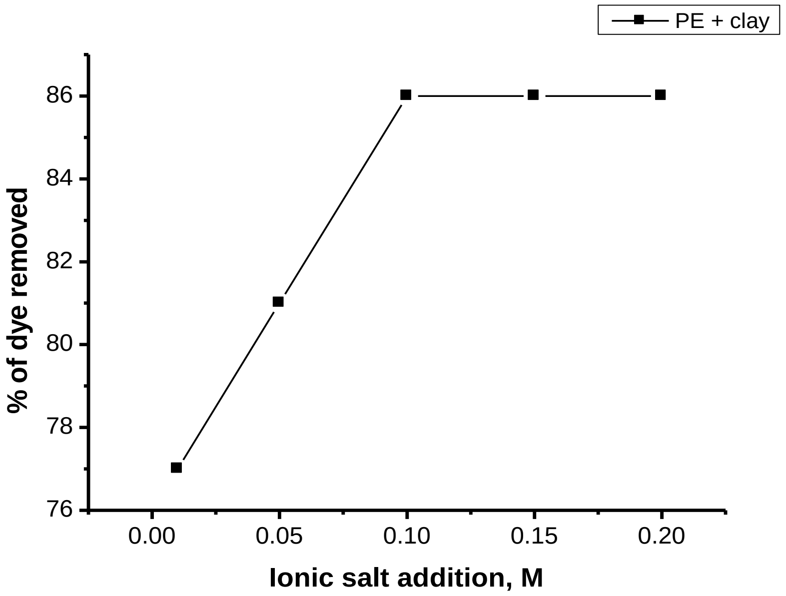

Figure (7) Effect of other ions on the adsorption of acid dye at dye conc. 50 mg/l ; contact time 120 min; adsorbent dose 10 g/l, temp. 25 °C.

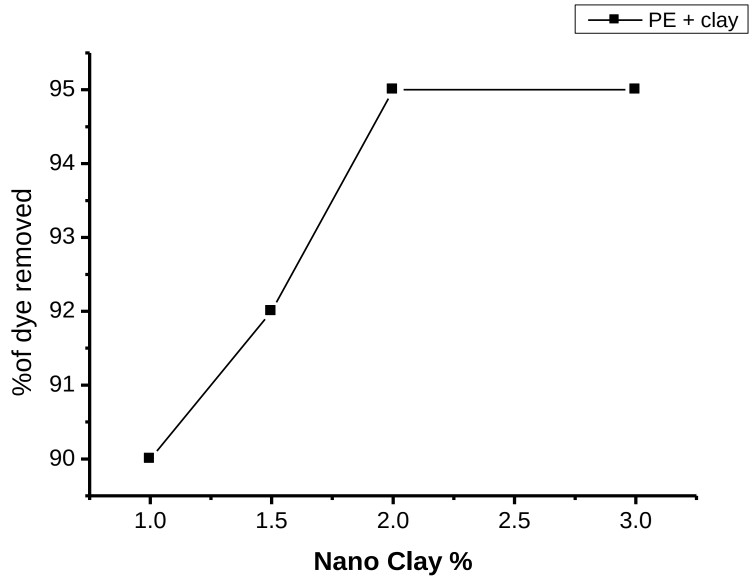

Figure (8) Effect of clay conc. on the adsorption of acid dye at dye conc. 50 mg/l ; contact time 120 min; adsorbent dose 10 g/l, temp. 25 ºC.

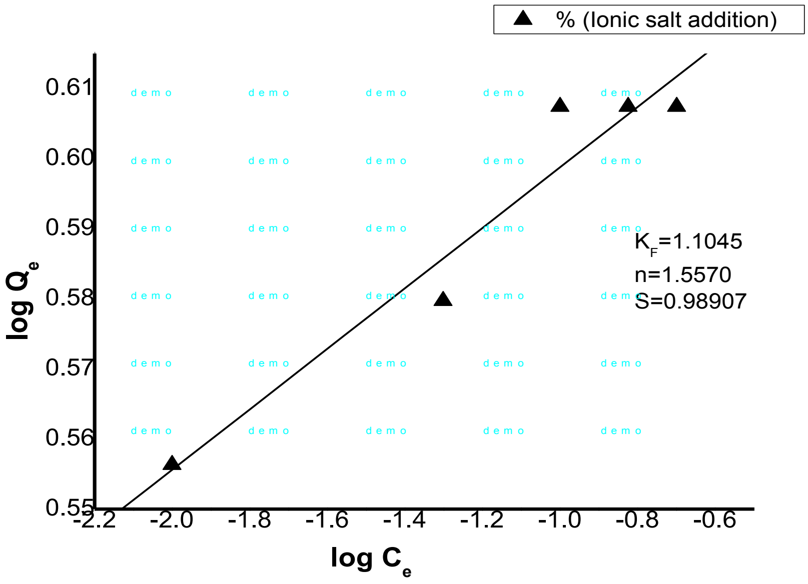

Figure (9) Linear Freundlich isotherm for the adsorption of dye by PE

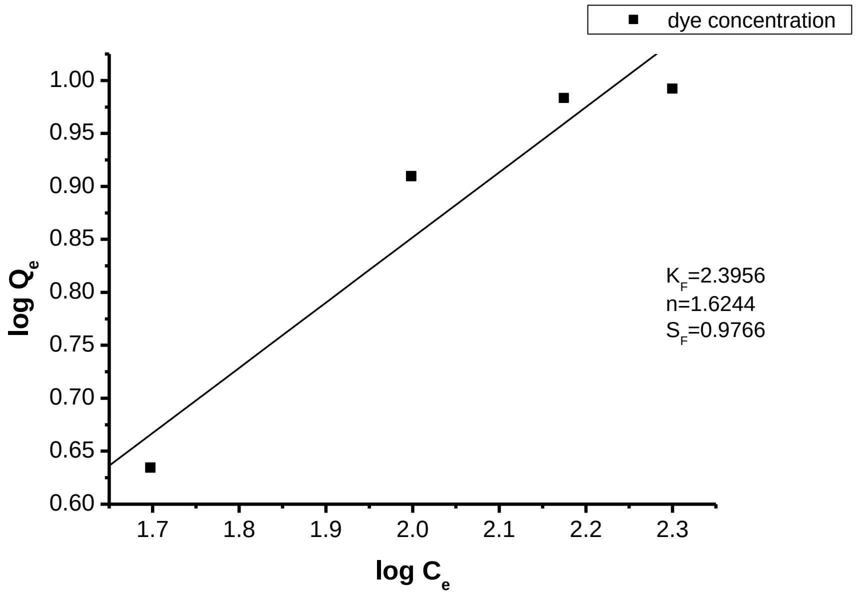

Figure (10) Linear Freundlich isotherm for the adsorption of dye by PE

Table (1) : **Equilibrium constant and thermodynamic parameters for the adsorption of Dye onto waste PE .**

Dye conc. mg/L	Temp.,^{0}C								ΔH	ΔS
	25	30	35	40	25	30	35	40		
	K_0				G^0					
50	0.02	0.06	0.1	0.2	9.3	6.8	5.7	4.0	26.7	81.9
100	0.01	0.03	0.05	0.1	10.9	8.5	7.8	5.7	26.7	80.8
150	0.006	0.02	0.033	0.066	11.9	9.5	8.4	6.8	26.6	79.5
200	0.005	0.015	0.025	0.05	12.6	10.2	9.1	7.5	26.7	79.5