

## **Kinetic modeling and equilibrium studies of selected endocrine disrupting chemicals on to low cost adsorbent**

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### **ABSTRACT**

*This research investigates the sorption properties of bisphenol A (BPA), 17 $\beta$  estradiol (E2) and 17 $\alpha$ -ethinylestradiol (EE2) in an aquatic environment by investigating the effectiveness of using batch and continuous processes. The adsorbents used were activated carbon of 2 mm and 0.4 mm diameter with powdered poly 1-methylperol-2-ylsquaraine (PMPs). They were applied to remove BPA, E2 and EE2 from aqueous solutions at a fixed concentration of 2 mg/l. The influence rate of agitation and dosage on EDCs removal and adsorption capacity was investigated by conducting a series of batch experiments. The adsorption equilibrium was achieved in 2 h with average percentage removal of 98.2 % ( BPA) 96.5 % ( E2) and 94.5 % ( EE2). The kinetic adsorption process could be described by pseudo-first order model by AC1 and intra-particle kinetics by PMPs. The adsorption constants were evaluated according to Langmuir, Freundlich, Temkin and D-R isotherm models. The experimental adsorption data were fitted to Langmuir and Freundlich adsorption model but best for Langmuir ( $R^2=0.99$ ).*

**Keywords:** Adsorption, Kinetics, Endocrine Disrupting Chemicals, Activated Carbon

### **INTRODUCTION**

Endocrine disrupting chemicals (EDCs) are organic pollutants that consist of synthetic and natural chemicals which affect the stability of normal hormonal functions in human and animals depending on their activity. According to [1] they are defined as a group of chemicals that can mimic normal endocrine functions either directly or indirectly through the interaction with receptor mediated processes like steroid hormone receptors even at low concentrations because of their steroid-like structure. Several studies have shown that humans and wildlife are exposed to a combination of multiple agent of EDCs due to the large variety of suspected EDCs [1]. Their effects are however versatile in both mammalian and non-mammalian species due to their various sources and how they are discharged to the environments. The main sources of these EDCs are air, water and soil. However, these endocrine disrupting chemicals are released into the environments basically through incomplete decomposition in municipal sewage treatment plants (MSTPs). Further studies have shown that EDCs can be categorized based on their pollutant sources from waste water treatments [2].

Quite a number of EDCs were detected in waste water effluents which includes largely estrogen disrupting chemicals (nonylphenol, 17 $\beta$ -estradiol and ethinylestradiol) and pharmaceuticals [3]. Furthermore, alkylphenols which includes (nonylphenol, octylphenol and nonylphenol ethoxylates), were also some of the EDCs discovered. In addition, bisphenol and nonylphenol are reported to be the most frequently found EDCs in water bodies [4].

Discovery of EDCs in sewage effluents and in the environment has generated some concern about their potential impact on ecological unit and human health. There are lots of evidences by researchers as a result of exposure to endocrine disrupting chemicals. The observed endocrine disrupting effects of developmental abnormalities in wildlife includes penis size reduction and testicular abnormalities in alligators by organochlorides in effluents; major cause of hermaphroditism in frogs is pesticides, feminisation of fish by effluent discharge by paper mills.

In contrary, some published reports have shown that effects of endocrine disrupting chemicals on human health such as poor semen quality and increase in cancer rates is as a result of casual relation between exposures to such chemicals [5]. Moreover, the defect in human has not been firmly established, except in isolated cases where a diethylstilbestrol (DES) which is a synthetic hormone, has been shown to cause developmental and reproductive problems [5].

According to [6], the choice of treatment processes depends on the desired receiving water characteristics, pollutants present in the untreated water with physical and chemical properties. [6] has investigated the development of activated carbon with a particular attention to advance treatments processes. Many advance treatment processes have been reported such as adsorption using activated carbon, membrane separation, reverse osmosis, microfiltration, and ultra-filtration and ion exchange techniques for treatment in different water analysis [6].

Poly 1-methylperol-2-ylsquaraine (PMPs) is blue black powder of spherical particles. According to previous researches, [7,8]. PMPs are prepared by refluxing equimolar amount of pyrrole derivatives and squaric acid in an alkyl alcohol (but-1-ol) for 16 hours. The cooled product was cooled and dried. Soluble small molecular weight materials were removed by repeatedly washing the product with ethyl acetate in a soxhlet for 16 hours.

Kinetic study of experimental data in adsorption processes helps to investigate the potential rate controlling mechanism such as mass transfer, chemical reaction and kinetic models [9]. There are several kinetic models that describes adsorption of endocrine disrupting chemicals (EDCs). This study will focus on the modelling sorption kinetics of BPA, E2 and EE2 onto activated carbon and PMPs using Langergren Pseudo first order, second-order Arrhenius kinetics and intra particle diffusion kinetics. Pseudo first and second order kinetic was proposed by Langergren which is expressed below as

$$\ln C/C_0 = -k_1 t \quad (1)$$

$$1/[C] - 1/[C_0] = k_2 t + Q \quad (2)$$

Where  $C_0$  = initial concentration (mg/l) and  $C$  = final concentration (mg/l)

Pseudo first order plot of  $\ln C/C_0$  against  $t$  should give a linear relationship from which  $k_1$  in ( $\text{min}^{-1}$ ) can calculated from the slope obtained from the graph.

Plot of  $1/[C] - 1/[C_0]$  against  $t$  will give a rate constant  $K_2$  of pseudo second-order adsorption in ( $\text{Lmg}^{-1}\text{min}^{-1}$ ).

One of the models to express the mechanism of solute adsorption onto an adsorbent is the intra particle diffusion kinetics in which the linear equation is expressed below:

$$q_t = K_{dif} t^{1/2} + C \quad (3)$$

According to this kinetics, a plot of  $q_t$  (mg/g) against  $t^{1/2}$  ( $\text{min}^{1/2}$ ) should be linear. However, if a straight line is obtained passing through the origin, it can be assumed that the mechanism involves the diffusion of the species and the slope of the linear curve is the rate constant of the intra particle transport ( $k_{dif}$ ) and if vice versa, this is an indicative of some degree of boundary layer control. It further shows that the intra particle diffusion kinetic is not the only control rate limiting step. In this research, there is no plot that passed through the origin and it has been proved by pseudo - first and second order kinetics. The deviation from the origin might be due to the difference in the mass transfer rate in both the initial and the final stage of the adsorption technique. The adsorption kinetics of activated carbon and PMPs onto bisphenol A (BPA),  $17\beta$  - estradiol (E2) and  $17\alpha$  - ethinylestradiol (EE2) was verified at concentration (2mg/l). The validity of intra particle diffusion kinetics model was determined by the use of sum of squared errors equation which is given below:

$$(\text{SSE, \%}) = \left\{ \sqrt{\frac{\sum [q_{e,\text{exp}} - q_{e,\text{cal}}]^2}{N}} \right\} \quad (4)$$

Where (N) is the number of data involved. The lower the SSE, the better a fit of the experimental data obtained.

**KINETICS MODELLING**

Kinetics is basically the rate of chemical reaction processes in an attempt to understand the basic concept that affect these rates and development of different theories and models to predict them [10]. To determine BPA, E2 and EE2 adsorption kinetics, four different kinds of kinetic models were applied: Lagergren pseudo first-order kinetics, Pseudo second order kinetics, Arrhenius kinetics and Intra-particle diffusion kinetic model

**Lagergren Pseudo-First-Order Kinetics**

The assumption involve in this kinetic is that the initial concentration of A is more than the concentration of B, which means that the change in A will not be significant during the reaction.

Pseudo-first-order kinetics is derived below:

From this reaction  $A + B \rightarrow P$

To obtain the differential form of rate law from reaction above

The rate of reaction of A is equal to

$$r_A = -\frac{d[A]}{dt} = k[A] \quad (5)$$

Where  $[A]$  = Concentration of reactant A. Substitute  $[A] = C$  in equation 14.

$$-\frac{d[C]}{dt} = k[C] \quad (6)$$

Integrating Eq. (6) with boundary conditions  $t = 1$  and  $t = 0$ ,  $C = C_0$  and  $C$  as shown in Eq. (7),

$$\int_{C_0}^C \frac{d[C]}{C} = -\int_0^t K dt \quad (7)$$

$$[\ln C - \ln C_0] = -Kt \quad (8)$$

$$\ln C / C_0 = -kt \quad (9)$$

Eq.(9) can be expressed in term of concentration which is expressed in Eq. (10) and (11) respectively.

$$\frac{dC}{dt} = K_1(C - C_0) \quad (10)$$

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (11)$$

Where  $t$  is the contact time (min),  $K_1$  = pseudo-first-order adsorption rate constant ( $\text{min}^{-1}$ ),  $q_e$  and  $q_t$  are the quantity of the adsorbate on the adsorbents at equilibrium in (mg/g) at time  $t$ .

$$\text{If } C/C_0 = A_0 \quad (12)$$

A graph of  $\ln C/C_0$  (mg/l) or  $\ln [A_0]$  against time (min) will be plotted and pseudo first order rate constant was calculated from the linear equation.

**Pseudo Second Order Kinetics**

The rate of a second order reaction is directly proportional to the square of the concentration of the reactant between A and B, such that

$A + B \rightarrow P$

$$\text{The rate of the reaction } r_{AB} = \frac{d[A]}{dt} = k[A][B] \quad (13)$$

If  $[A] = [B]$

$$\frac{d[A]}{dt} - k[A]^2 \quad (14)$$

By separating the variables and integrating Eq. (14) with boundary conditions  $t = t$  and  $t = 0$ ,  $A = A$  and  $A_0$ :

$$\int_A^{A_0} \frac{d[A]}{[A]^2} = - \int_{t_0}^t K dt \quad (15)$$

$$\frac{1}{[A]} = Kt + C \quad (16)$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = Kt \quad (17)$$

A graph of  $\frac{1}{[A]}$  in (mg/l) against time (min) was plotted and pseudo – second - order rate constant was evaluated from the linear equation.

### Arrhenius Kinetics

Arrhenius equation is also a useful kinetic equation in the thermodynamic parameters determination. This equation is frequently express in the logarithm form as shown below in equation (19);

$$\ln k = \frac{Ea}{RT} + \ln A \quad (18)$$

A graph of  $\ln k$  against  $\frac{1}{T}$  gives a straight line graph of linear equation

$$y = -mx + b \quad (19)$$

Where  $y = \ln k$ ,  $m = -\frac{Ea}{R}$ ,  $x = \frac{1}{T}$  and  $b = \ln A$

Where  $k$ = rate constant for the reaction,  $Ea$  = the Arrhenius activation energy of adsorption,  $A$ = Arrhenius frequency factor,  $R$  = gas constant (8.314J/molK),  $T$  = temperature (kelvin)

### Intra Particle Diffusion Kinetics Model

Adsorption of BPA, E2 and EE2 onto PMPs powders and activated carbon could be controlled through external film diffusion at the early stage of adsorption. The likelihood of intra – particle diffusion resistance was identified by using the kinetic model shown in equation (20)

$$q_t = K_{dif} t^{1/2} + C \quad (20)$$

A graph of  $q_t$  against  $t^{1/2}$  and  $K_{dif}$  are determined from the slope of the regression line. Where  $q_t$  = sorption capacity (mgg<sup>-1</sup>)  $K_{dif}$  = intra-particle diffusion rate constant (mgg<sup>-1</sup>min<sup>-1/2</sup>)  $t^{1/2}$  = time interval (min<sup>-1/2</sup>)  $C$  = intercept

## MATERIALS AND METHODS

The experiment was geared towards the determination of the kinetic properties of PMPs in the removal of EDCs from waste water and also to compare it effectiveness with GAC and PAC. In the experiment, emphasis was laid on BPA, E2 and EE2 due to their impact in the environments. These compounds were spiked in distilled water (D1) at different concentrations. Granulated activated carbon (AC1) of different particle sizes and PMPs were used as adsorbents in order to describe both the adsorption equilibrium and isotherms of different adsorption systems. The experiment was carried out using different controlled temperatures in order to evaluate adsorption thermodynamics. High performance liquid chromatography (HPLC) was used for both the qualitative and quantitative analysis after various treatments.

### Materials and Reagents

Materials used for the research are as follows: Hot air oven, Desiccators, Orbital Shaker, Filter paper, micropipette, Ice, cotton wool, foil paper, peristaltic pump, retort stand, weighing balance, thermostated water bath, sieves, HPLC and experimental glass wares. Granulated activated carbon (AC1) of 2.00mm particle size, powdered activated carbon(AC2) of 0.4mm particle size, and PMPs (powdered form) were used as adsorbents.

### Research Stock Solution

1000ppm stock solution of BPA, E2 and EE2 were prepared by weighing 0.2g of each solute in different 200ml volumetric flask that contains methanol. The separate stock solution was swirled and made up to the graduated mark with deionised water. These were transferred in clean labelled amber bottles and kept in a laboratory refrigerator.

### Effect of Different Contact Time

After thermal regeneration on the adsorbents for 24hrs at 120<sup>0</sup>C. The selected dosage of adsorbents was used to adsorb BPA, E2 and EE2 at the optimum concentration of 2ppm. Each conical flask contained different weight of adsorbents PMPs, AC1, AC2 and 50ml of adsorbates solution. All conical flasks were shaken at a speed of 10 rpm at room temperature 22 <sup>0</sup>C and different contact time of 10, 20,30,60,90 and 120 min in order to obtain the best contact time of the adsorption treatments. The samples were subjected to HPLC analysis.

### Effect of Different Masses

The selected masses of PMPs, GAC and PAC were used to adsorb BPA, E2 and EE2 at a concentration of 2ppm in 200ml conical flask. The masses 0.05,0.1,0.2,0.4 and 0.8 g were carefully weighed with a weighing balance (Sartorius Aggottingen, Germany) in five different 200 ml conical flask and the flasks were shaken at room temperature. The samples were analysed after adsorption treatments using HPLC.

The initial concentration and equilibrium concentration after adsorption ( $C_i$  and  $C_e$ ), dry weight of adsorbent ( $w$ ), and volume of aqueous solution ( $l$ ). The amount of equilibrium adsorption of BPA, EE2 and E2 was determined using Eq. (21) :

$$q_e (mg g^{-1}) = \frac{(C_i - C_e)(mg / l)}{W(g)} v(l) \quad (21)$$

### Kinetic Study

A 0.4g of the adsorbent AC1, AC2 and PMPs were weighed and transferred into 200ml conical flask. 1ml of the adsorbate was measured into 50ml volumetric flask to obtained 2mg/l concentration of BPA, E2 and EE2. These mixtures were agitated at speed 200 rpm for 2 h at different controlled temperatures 15 <sup>0</sup>C, 20 <sup>0</sup>C, 25 <sup>0</sup>C and 30 <sup>0</sup>C respectively. At the end of the agitation, the suspensions were separated by filtrations through 70mm diameter filter paper, the filtrates were subjected for analysis using HPLC.

The kinetic models employed for this study was : Lagergren pseudo first-order kinetics, pseudo second order kinetics, Arrhenius kinetics, intra-particle diffusion kinetic model and the adsorption isotherms used: Lagmuir, Freundlich, Temkin and Dubinin – radushkevich adsorption isotherms using the equilibrium data from the models.

### Adsorption Isotherm

Adsorption isotherm or data from equilibrium modelling is basically use to explain the interaction of solute or the analyte with the adsorbents and is significant in optimizing the use of adsorbents. The amount of adsorbate that can be taken up by an adsorbent as a function of pressure (gas) and concentration (liquid) at steady temperature is the adsorption isotherm. There are several equations or models that can be used to describe this function [11].

In this study, Lagmuir, Freundlich, Temkin and Dubinin – Radushkevich isotherms will be used to describe the sorption capacity of the adsorbate onto the adsorbent by linear regression and the best equation that describe the adsorption isotherm of PMPs .

### Laboratory Data Chemical Analysis

Percentage recovery of BPA, E2 and EE2 were obtained using the relationship below:

$$\% \text{ recovery} = \frac{C_0 - C_e}{C_0} \times 100 \quad (22)$$

Where  $C_0$  = Initial concentration (mg/l)  $C_e$  = Equilibrium concentration (mg/l)

Instruments Quantization Limit (IQL), Limit of detection (LOD) and Relative standard deviation (RSD) are important parameters for laboratory analysis

These parameters are defined below:

$$\text{Instruments Quantization Limit (IQL)} = 10\sigma/S \quad (23)$$

$$\text{Limit of detection (LOD)} = 3.3\sigma/S \quad (24)$$

$$\text{Relative standard deviation (RSD \%)} = \sigma_{n-1}/\text{mean} \times 100 \quad (25)$$

Where  $\sigma$  is the standard deviation and slope obtained from the calibration plots

## RESULTS AND DISCUSSION

The removal rate of the adsorbates in respect to the quantity of adsorbents and contact time with different reaction temperatures of a fixed initial concentration was studied. The effects of the dose and contact time of the systems were also studied. Mass Transfer Zone (MTZ) and the breakthrough were evaluated. Langmuir, Freundlich, Temkin and Dubinin – radushkevich are significant adsorption isotherm in the study.

### Effect of Adsorbent Dose

The results obtained from the batch adsorption process in comparison to the PMPs indicate that with high adsorbent dose, there is an increase removal rate of EDCs. The results show that the adsorption of the adsorbates increases in the amount of adsorbents due to greater availability of the surface area at higher concentration of the adsorbents.

Activated carbon with 2.00 mm particle size was the most efficient with a dose of 0.8 g gives removal of 98.20 % for BPA, 96.55 % for EE2 and 94.45 % for E2 and PMPs gave removal of 96.9 % BPA, 94.7 % EE2 and 92.81 % for E2 but AC2 was effective in removing EE2 and E2 with percentage removal of 92.34 % and 91.62 % .BPA gave the least % removal of 86.50 % as shown in Fig 1.- Fig .3

Where AC1 = Activated carbon (2mm particle size)

AC2 = Activated carbon (0.4mm particle size)

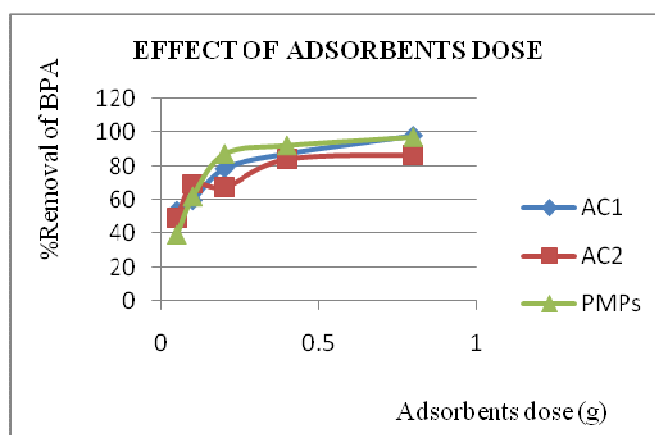


Fig 1. BPA effect of adsorbent dose

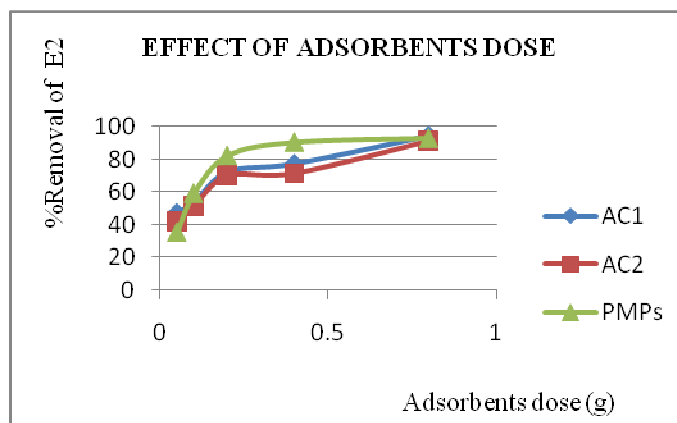


Fig 2 E2 effect of adsorbent dose

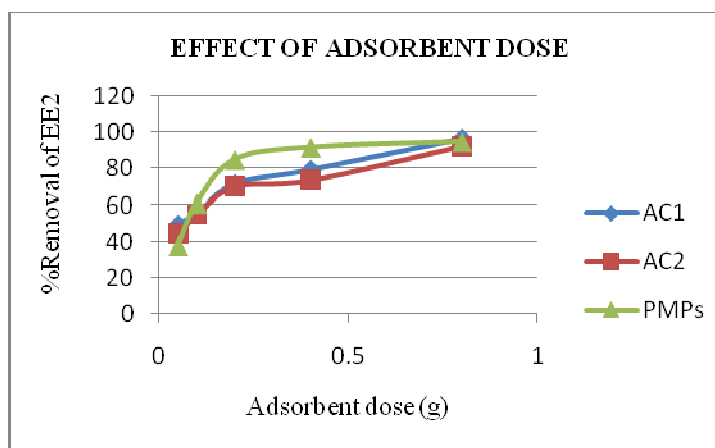


Fig.3 EE2 effect of adsorbent dose

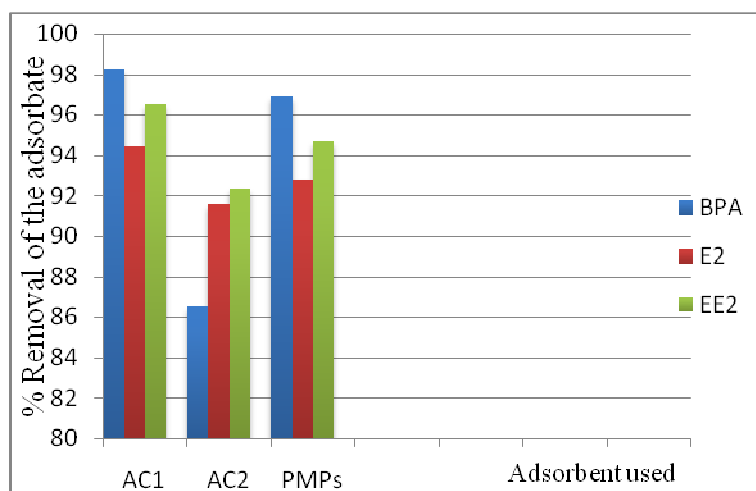


Fig. 4 Trend of the removal efficiency

From Fig. 4, the results can be summarised and the trend in the removal efficiency of the adsorbents can be compared as follows: For comparison of activated carbon (2 mm) in the % removal of the adsorbate, the trend is AC1>PMPs>AC2 and is the same for PMPs. For 0.4 mm activated carbon (0.4 mm) in the removal of adsorbate, the trend is EE2>E2>BPA

The difference in adsorption is attributed to the low ash contents in the carbon sample (AC2) which increases the adsorption capacity because of the hydrophilic nature of E2 and EE2. The ash content in AC1 is higher which has more affinity for BPA than E2 and EE2.

#### Effect of Contact Time

Adsorption of adsorbates; BPA, E2 and EE2 were measured at fixed concentration of 2 mg/l of different contact time of 10, 20, 30, 60, 90 and 120 min. From Fig. 5, 6 and 7 below show higher percentage removal of the adsorbate at higher contact time. It was also revealed that the percentage of the adsorbates removal was higher at the beginning for AC1 which gave an average of 51%; this is probably due to a larger surface area of the AC1 and PMPs available at the beginning for the adsorption of the adsorbate at the best contact time (120 min). From the plots equilibrium time has just been attained which is clearly shown in further increase of contact time. But from the results obtained from 30 – 60 min for AC1 in the removal of BPA, the removal rate is 49.5% – 85.5% but from 90 – 120 min for the same adsorbent shows a drastic decrease from 94.5% – 98.2%. For AC1 in the removal of E2 and EE2. And the trend is the same for all the adsorbents – adsorbate interactions as shown in the Fig. 5, 6 and 7 respectively. The surface adsorption sites are becoming exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Increase in contact time increases the rate of adsorption and it remains constant after equilibrium was reached in 120 min for a fixed initial concentration of 2 mg/l.

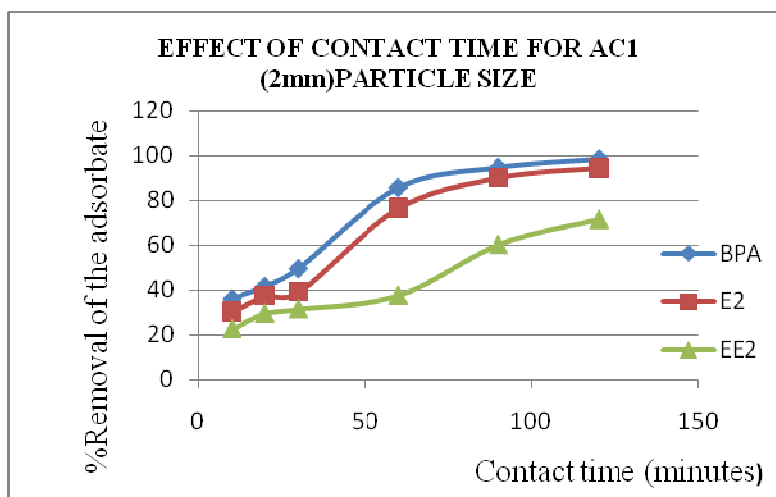


Fig.5 The effect of contact time with adsorbent AC1

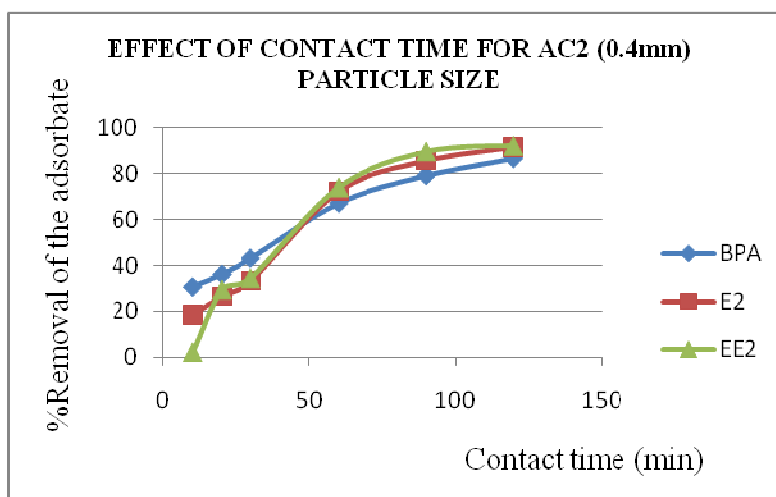


Fig.6 Effect of contact time with adsorbent AC2

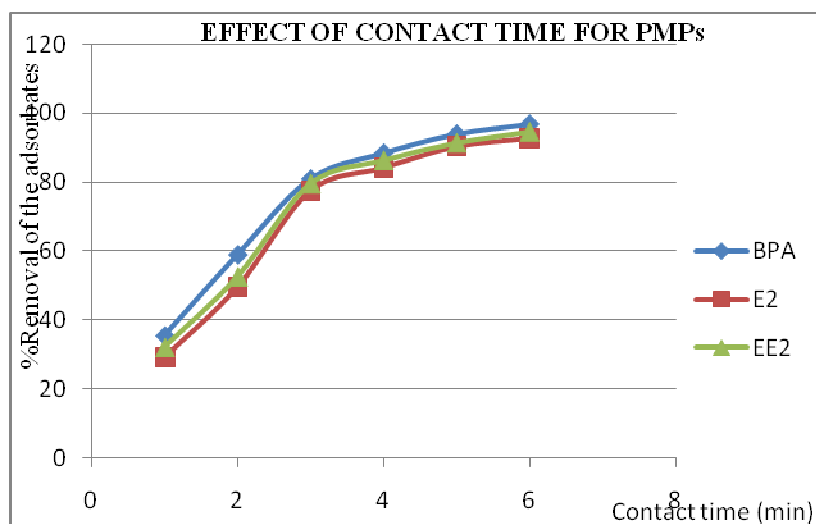


Fig.7 Effects of contact time with adsorbent PMPs

### Adsorption Kinetic Study

The results of fitting experimental data with the pseudo first-order and pseudo second-order models for the adsorption of BPA, E2 and EE2 onto activated carbon and PMPs will be compared in Table 1. This shows a critical



comparison of both pseudo first and second order kinetics in terms of rate constants  $K_1$  and  $K_2$  with their corresponding correlation coefficients  $R^2$

Table 1 Pseudo first and second-order kinetic of adsorbent AC1

Adsorbate	Pseudo-first order kinetics			Pseudo-second order kinetics		
	Equation	K	$R^2$	Equation	K	$R^2$
BPA	$y = -0.0369x + 0.3787$	0.0369	0.995	$y = 0.1433x - 4.256$	0.1433	0.969
EE2	$y = -0.0305x + 0.3120$	0.0305	0.998	$y = 0.0769x - 2.167$	0.0769	0.965
E2	$y = -0.0303x + 0.4021$	0.0303	0.999	$y = 0.0705x - 2.066$	0.0705	0.954

Table 2 Pseudo first and second-order kinetic of adsorbent AC2

Adsorbate	Pseudo-first order kinetics			Pseudo-second order kinetics		
	Equation	K	$R^2$	Equation	K	$R^2$
BPA	$y = -0.0166x - 0.0787$	0.0166	0.997	$y = 0.0251x - 4126$	0.0251	0.992
EE2	$y = -0.0297 - 0.4584$	0.0297	0.999	$y = 0.05x - 1.3490$	0.0500	0.983
E2	$y = -0.0256x - 0.3276$	0.0256	0.992	$y = 0.0456x - 2217$	0.0456	0.985

Table 3 Show the pseudo first and second-order kinetic of adsorbent PMPs

Adsorbate	Pseudo-first order kinetics			Pseudo-second order kinetics		
	Equation	K	$R^2$	Equation	K	$R^2$
BPA	$y = -0.0196x - 1.0251$	0.0196	0.996	$y = 0.0962x - 1875$	0.0962	0.954
EE2	$y = -0.0147x - 1.1346$	0.0147	0.998	$y = 0.0574x + 0.0559$	0.0574	0.974
E2	$y = -0.0144x - 1.0306$	0.0144	0.985	$y = 0.050x - 0.0042$	0.050	0.948

Tables 1, 2 and 3 present constant values and correlation coefficient  $R^2$  of both pseudo first – order and pseudo second – order kinetic models for adsorption of BPA, EE2 and E2 onto the AC1, AC2 and PMPs respectively. And since a higher value of correlation coefficients shows more suitable condition. The values of correlation coefficient ( $R^2$ ) of pseudo first-order kinetic model were better than pseudo-second order kinetic model with decreasing rate constants. Pseudo first-order model on activated carbon is relatively higher and ranges from 0.995-0.999 for the removal of the three adsorbents. While for PMPs, the  $R^2$  is slightly lower than that of the AC1 and AC2 and ranges between 0.985 – 0.996.

On the other hand, the correlation coefficients for pseudo second order kinetic are low compared to pseudo-first order kinetic as it ranges between 0.948 – 0.992 but still have a better correlation coefficients for AC1 and AC2 than PMPs with a range of 0.969 – 0.999. It has been observed that for both kinetic models, the fit of the experimental data of PMPs is quite low compared to activated carbon. The difference of the adsorbents may be attributed to lower competition for the sorption surface sites at lower concentration. Similar observation was reported by [11].

In this research, there is no plot that passed through the origin and it has been proved by pseudo - first and second order kinetics. The deviation from the origin might be due to the difference in the mass transfer rate in both the initial and the final stage of the adsorption technique. From Fig.5, 6, and 7 it can be seen that there are three sections from the graphs; steady and fast stage, curve and the last stage(straight).The steady stage may be considered as the fast adsorption stage which always take place at the surface, the second stage is where the intra-particle diffusion kinetics is controlled and the last stage is where intra particle diffusion kinetics start to slow down as a result of the adsorbate concentration that was small in the solution (2mg/l). In the intra particle diffusion kinetic stage where the adsorption technique takes place, there might be a limited uptake due to the size of the adsorbate molecules (BPA, E2 and EE2) the concentration of the adsorbate and its affinity to the adsorbent (activated carbon and PMPs). The diffusion coefficient of the adsorbate in the bulk phase, the distribution of the adsorbent pore size as well as the degree of mixing of the aqueous solution also contributed to the limited uptake. The correlation coefficients ( $R^2$ ) values obtained from the intra particle diffusion plots are lower than the correlation coefficients for both pseudo first and second – order kinetics.

#### Validity of Intra Particle Diffusion Kinetics

The adsorption kinetics of activated carbon and PMPs onto bisphenol A (BPA), 17 $\beta$  – estradiol (E2) and 17 $\alpha$  – ethinylestradiol (EE2) was verified at concentration (2 mg/l).The validity of intra particle diffusion kinetics model was determined by the use of sum of squared errors equation which is given below:

$$SSE, \% = \left\{ \sqrt{\frac{\sum [q_{e,exp} - q_{e,cal}]^2}{N}} \right\}$$

Where N is the number of data involved. The lower the SSE, the better a fit of the experimental data obtained. Table 4, 5 and 6 show the list of adsorbents (AC1, AC2 and PMPs) and adsorbates (BPA, E2 and EE2) with their corresponding SSE R<sup>2</sup> values.

**Table 4 Validity of intra particle diffusion kinetic model by adsorption onto AC1**

t <sup>1/2</sup> (min)	Adsorbate	Equation	R <sup>2</sup>	SSE, %
5.4772	BPA	y = 0.2572x-1.431	0.9049	0.65
7.74596	E2	y = 0.129x-0.7056	0.9167	0.33
9.48683	EE2	y = 0.1424x-0.7701	0.9298	0.37

**Table5 Validity of intra particle diffusion kinetic model by adsorption onto AC2**

t <sup>1/2</sup> (min)	Adsorbate	Equation	R <sup>2</sup>	SSE, %
5.4772	BPA	y = 0.0463x-0.214	0.9736	0.13
7.74596	E2	y = 0.084x-0.4467	0.9604	0.20
9.48683	EE2	y = 0.1217x-0.6731	0.9047	0.34

**Table 6 Validity of intra particle diffusion kinetic model by adsorption onto PMPs**

t <sup>1/2</sup> (min)	Adsorbate	Equation	R <sup>2</sup>	SSE, %
5.4772	BPA	y = 0.0879x-0.379	0.9168	0.31
7.74596	E2	y = 0.0463x-0.1607	0.9093	0.17
9.48683	EE2	y = 0.0527x-0.1803	0.9449	0.22

Comparison of BPA, E2 and EE2 uptake for each adsorbent indicates the superiority of the AC1 and AC2 over PMPs polymer. The highest uptake was observed for PMPs with SSE values of 0.31, 0.17 and 0.22 respectively. Comparing tables 4, 5 and 6 above, it can be seen that BPA, E2 and EE2 molecules were removed faster by finer particles of PMPs than the coarse particles of AC1 and AC2. The intra particle diffusion kinetic model has been used for other applications for organic and inorganic removal by spherical adsorbents from aqueous solutions [12]. The sum of squared errors (SSE) reported were of the same order of magnitude with the trend of this study. The SSE values obtained in the study ranges from 0.3 – 0.7 which agree with the values for the removal of phenol using activated carbon. Kinetic models that have been applied to remove oestrone by activated carbon are very few. The intra particle kinetic summary trend of the study (PMPs>AC2>AC1)

## CONCLUSION

The adsorption behaviour of BPA, E2 and EE2 on activated carbon and PMPs were investigated in batch process which was found to be largely dependent on adsorbent dosage and contact time. The adsorbate-adsorbent interactions attained equilibrium in 120 min.

Langmuir, Freundlich, Temkin and Dubinin – Radushkevish Isotherms were applied to equilibrium data at optimum amount of adsorbent (0.4g). Langmuir and Freundlich isotherm were fitted more than Temkin and da-radushkevish isotherm at different temperatures of BPA, E2 and EE2 onto AC1, AC2 and PMPs.

Analyses of pseudo first - order, pseudo second- order and intra particle kinetic models show that kinetics of BPA, E2 and EE2 onto AC1, AC2 and PMPs are best described by pseudo first - order than pseudo-second order model. While those of BPA, E2 and EE2 onto PMPs are best described by intra – particle model.

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