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Operational factors effects on thermodynamics of arsenic removal from aqueous solutions

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Abstract-This paper presents the mechanism and thermodynamics of adsorption of arsenic (AsaC) onto powdered eggshells (PWES). Natural and unprocessed eggshells were collected from ObafemiAwolowo University agricultural farm, Ile-Ife, Nigeria. These natural and unprocessed eggshells were cleaned using distilled water, air-dried, pulverised into powder, separated according to sieve sizes using British Standard sieves and stored in desiccators. The elemental contents and micrograph structure of the PWES were determined using standard methods. Adsorption kinetics of AsaC onto PWES were monitored using standard adsorption kinetics models. Effects of pH, particle size, mass of adsorbent and initial AsaC concentrations on the adsorption. Thermodynamic of AsaC adsorption onto PWES were studied and analysed using analysis of variance (ANOVA). The study revealed that contained Si, Fe, Al, Ca, C, K and O. It has pores at various levels. Initial concentration of AsC was a significant factor in removing AsC from water using PWES at 95 % confidence level ($F_{3,4}$ = 10.24, p = 0.02). Thermodynamic parameters entropy (ΔSo),Gibbs free energy (ΔGo) and enthalpy (ΔHo) were in range of -67.67 to 117.58 J/mol.K, -35.52 to 20.53 J/mol.K and 0.43 to 105.94 J/mol.K.h, respectively. It was concluded that thermodynamics studies with modified Van'tHott's equation revealed that the adsorption process was endothermic and has strong affinity for AsaC.

Keywords:*Investigation, fish farming, fresh water, food, southern Algeria.*

1. Introduction

Access to safe and potable water is one of the most significant determinants of health and socio-economic development of any community [1]. The importance of potable and safe water supplies had led to an importance on the establishment of suitable facilities in developing countries [1 - 4]. The drinking of AsC contaminated water origins adverse influences on human health, which in-return deteriorates socio-economic status of the people. In addition, consumption of AsCcontaminated water and food not only marks in more sickness and death, but origins higher health care cost, low productivity, lower school enrolment, and enlarged poverty [1, 5]. Removal of AsaC contamination from water and wastewater can be accomplished by a variety of techniques such as: coagulation [6], adsorption [7,8], ion exchange, filtration, reverse-osmosis, electrochemical, precipitation [9], membrane filtration , electro-dialysis [10] and biological process [11]. With exception of adsorption and filtration AsaC removal technologies mentioned are not sustainable for rural community in developing countries because of high capital cost and maintenance by skilled labors, thereby making adsorption the most economical and easy to implement for AsaC removal [12]. The development of environmental and user-friendly AsC removal machineries has gained noteworthy attention of the scientific communities In the recent years, the use of adsorbent (biochar) for removal of AsC, heavy metals and several other toxic elements from contaminated wastewaters and water has been recognised as extremely cost-efficient and eco-friendly technique [2,4]. More on AsaC removal and treatment can be established in An et al. [9], Analia et al. [13]; Bozas and Boz [14], Doina et al.[15], Alam et al. [16], Nena et al. [17]; Shih [10]; Zunaira and Zhu [18]; Mirjana et al. [19]; Largittea and Pasquierta [20]; Seda et al. [21] and Tural et al. [22] . The principal objective of this study was to investigate adsorption capacity of powdered eggshell (PWES) with particular attention to adsorption thermodynamic of AsaC reactions.

2. Materials And Methods

Natural and unprocessed eggshells (chicken) were collected from Agricultural Farm, ObafemiAwolowo University, Ile-Ife, Nigeria. These raw eggshells were cleaned using distilled water (to remove impurities and sand), air-dried, pulverised into powder and separated into various sizes using British Standard sieves. These powdered raw eggshell with sieve sizes of lower than 63 x 10-6 m (PWES1), between 63 x 10-6m and 75 x 10-6m (PWES2) and between 75 x 10-6m and 150 x 10-6m (PWES3) were separated and stored in desiccators. The elemental contents of the PWES were determined using Atomic Absorption Spectrophotometer (AAS) after acid digestion of a known mass of the samples [23, 24]. The microstructure was examined using a scanning electron microscope (Carl Zeiss Smart Evo 10). This was carried out with the aid of the backscattered electron detector, providing compositional contrast and the secondary electron detector providing topographical information. Energy Dispersive Spectroscopy (EDS) was used to confirm the elemental composition of identified phase while examinations were done in the high vacuum mode. Selected physical and chemical properties of the PWES were determined using standard methods. The detailed methods are presented in another paper [25, 26]. Adsorptive rates of synthetic wastewaters and natural waters (raw water form Aponmuriver, artificial lake in Elizade University, Ilara - Mokin, water samples were collected weekly for four months) were monitored. The amount of solute remove (adsorbed) was computed using equation (1).

$$q_t = \frac{(C_0 - C_t)}{M}V \quad (1)$$

Where: $q_t$is the adsorption capacity of the PWES at any time t; (mg/g), C_0 is initial the concentration of AsaC in the solution (mg/l), C_t is the experimental concentration of AsaC in the solution at time t (mg/l).

Impacts of pH, particle size, mass of the adsorbent and initial concentrations on the adsorption capacity of AsC onto the PWES were evaluated using ANOVA [3]. Thermodynamic parameters (enthalpy, ΔH^o, entropy, ΔS^o, and free Gibbs energy ΔGo) of adsorption kinetics of AsaC onto PWES were computed based on experiments performance in a batch system at time between 1 and 12 hours as follows [27, 28, 30] :

$$\ln(1000K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

$$K_d = \frac{q_t}{C_t} \quad (3)$$

$$\Delta G^O = \Delta H^o - T\Delta S^o = -RT\ln(100K_d) \quad (4)$$

where R is the universal gas constant (8.314 J mol−1 K−1), T is the temperature (303K). K_d is the distribution coefficient. Effects of selected factors were analysed statistically using analysis of variance (ANOVA).

3. Results And Discussion

The detailed of result of the composition determination was presented in another paper The results of scanning electron microscope, backscattered electron detector and the secondary electron detector are as presented in Figure 1. Figures 1a, b and c revealed that PWES has pores at various levels and at different sizes. Figures 2a, b and c established that with literature [29, 30 and 31]. These results indicated that PWES has ability to adsorb dissolved minerals in the aqueous state. Figures 1d, e, f and g revealed that PWES contained Si, Fe, Al, Ca, C, K and O. The results revealed that the PWES is a calcium salt (calcite material). Figure 2d affirmed this composition of PWES [30]. However, percentage of these elements varied. It has been suggested that in the present of water aluminum, calcium and iron salts underwent displacement reactions. These results show that the PWES underwent the reaction in equation (5) with AsaC, which altered the pH value and the product formed react with arsenic ion to precipitate the pollutant as calcium, aluminum and iron salts.

$$Ca(OH)_2 + X_2HAsO_4 \rightarrow CaHAsO_4 + 2XOH \quad (5a)$$
$$Fe(OH)_2 + X_2HAsO_4 \rightarrow FeHAsO_4 + 2XOH \quad (5b)$$
$$Al(OH)_3 + 3X_2HAsO_4 \rightarrow Al(HAsO_4)_3 + 6XOH \quad (5c)$$

Figure 3 shows relationship between qe, mass of the adsorbent added and Ce. These figures Figure 3 a and b) indicated that there are relationship between these three parameters, which will help in the selection of operational factors. This observation agrees with literature on adsorption kinetics of AsC onto adsorbent [4 -8].

Thermodynamic Parameters: The thermodynamic parameters provide in-depth information about the energetic changes associated with adsorption process. Values such as standard Gibbs energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) for the adsorption of the AsaC onto PWES were determined using modified Van'tHott's plots of equation (2). Table 1 presents calculated values of thermodynamic parameters. Thermodynamic parameters ΔS°, ΔG° and ΔH° were in range of -67.67 to 117.58 J/mol.K, -35.52 to 20.53 J/mol.K and 0.43 to 105.94 J/mol.K.h, respectively. Positive values of ΔH° indicate the endothermic nature of the adsorption process. The value of ΔH° becomes more positive with decreasing particle size indicating that a decrease in particle size of PWES favors the removal process. The positive ΔH° values at different factors (initial concentrations, pH, particle sizes and mass of adsorbent) indicate the endothermic nature of the adsorption of AsaC on PWES. The negative values of ΔG° at different factors (initial concentrations, pH, particle sizes and mass of adsorbent) indicate the spontaneous nature of the adsorption of AsaC on PWES, which indicate that the sorption process is spontaneous in nature and the adsorbent has a great affinity towards the AsaC [31]. The positive values of ΔS° at different factors (initial concentrations, pH, particle sizes and mass of adsorbent) indicate the endothermic nature of the adsorption of AsaC on PWES indicate that the sorption process is endothermic in nature and the adsorbent has a great affinity towards the AsaC [32, 33 and 34].

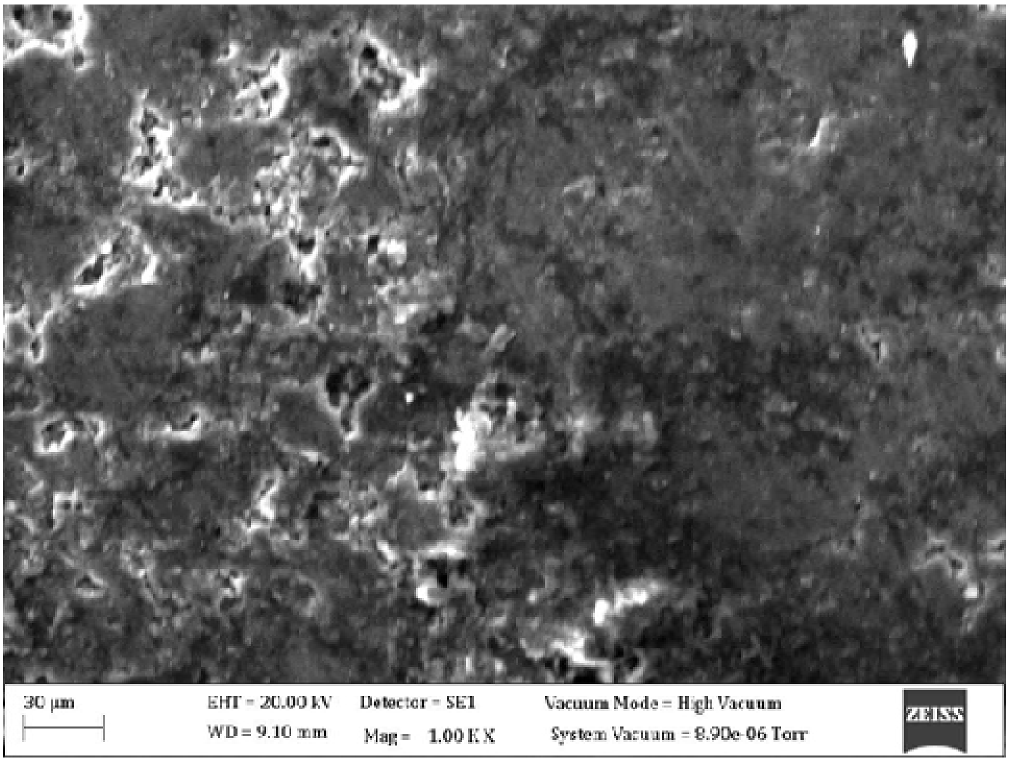

Figure 1a: SEM of PWES magnitude 1.00 KX

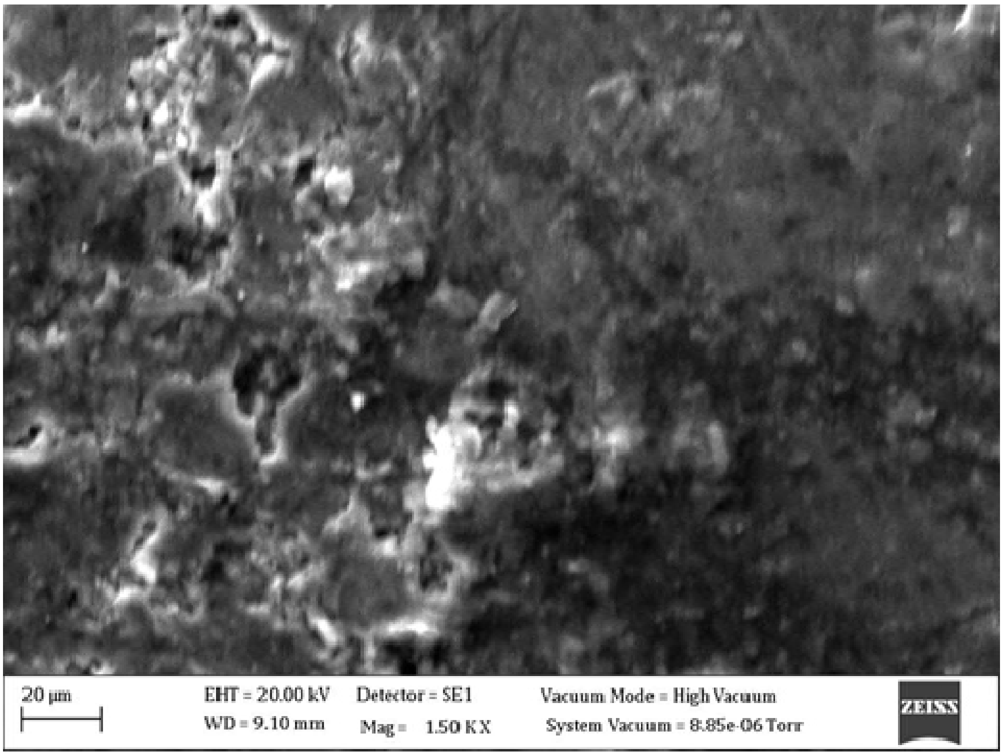

Figure 1b: SEM of PWES magnitude 1.50 KX

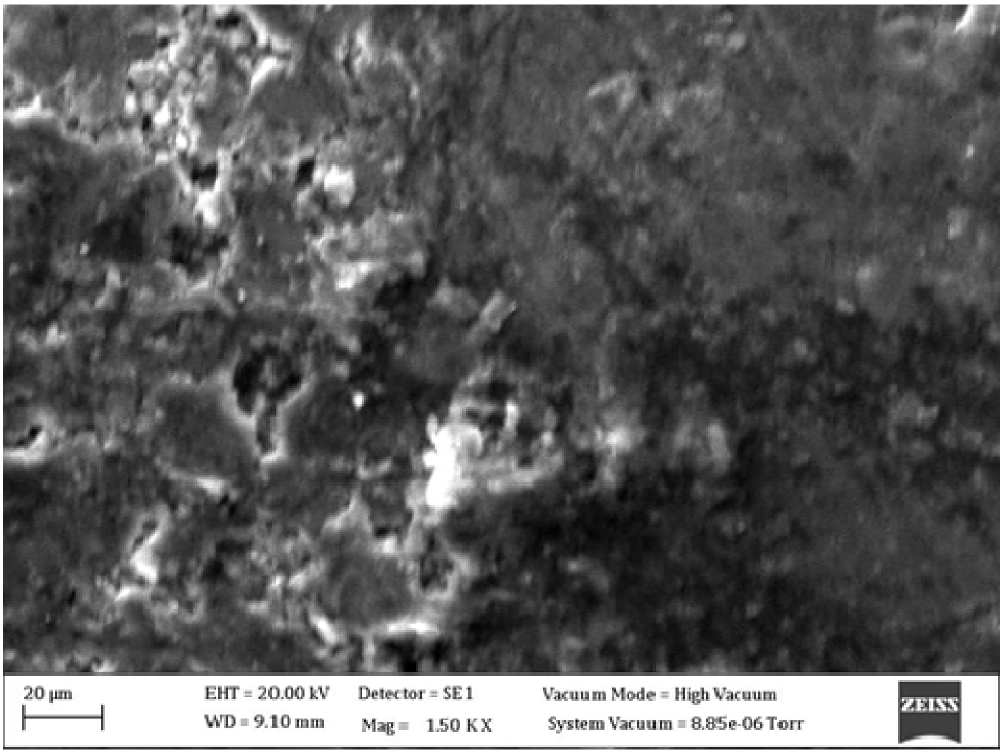

Figure 1c: SEM of PWES magnitude 1.50KX

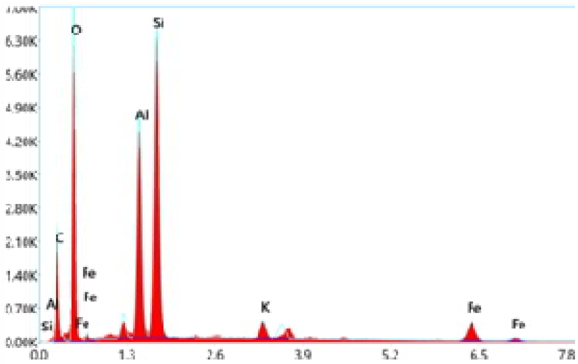

Figure 1d: EDS of Spot 3 of PWES for composition

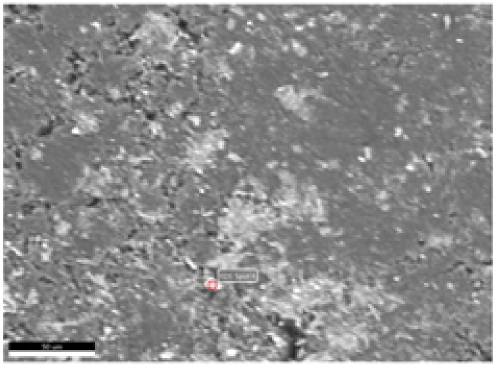

Figure 1e: Spot 3 of PWES for composition

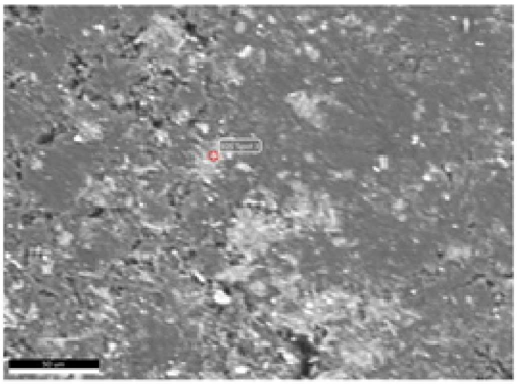

Figure 1f: Spot 8 of PWES for composition

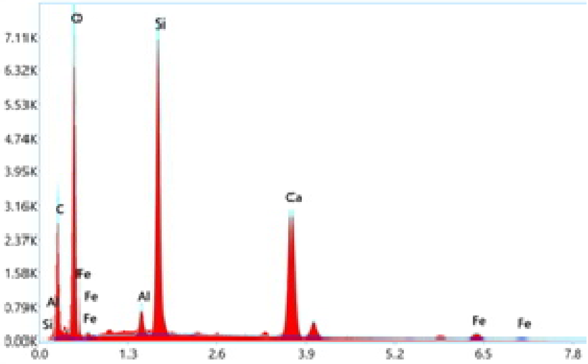

Figure 1g: EDS of Spot 8 of PWES for composition

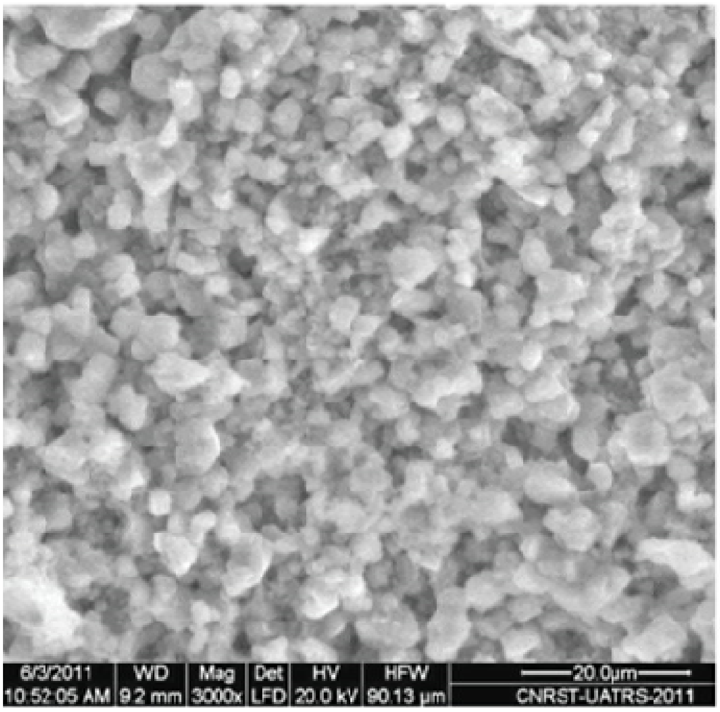

Figure 2a: Similar SEM of PWES [29].

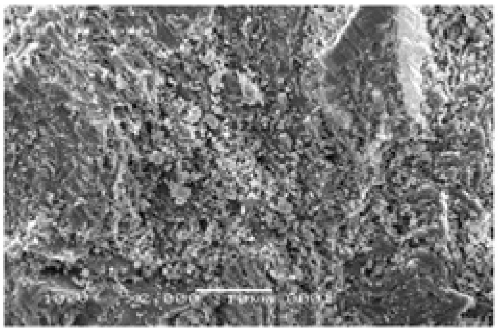

Figure 2c: Similar SEM of PWES [31].

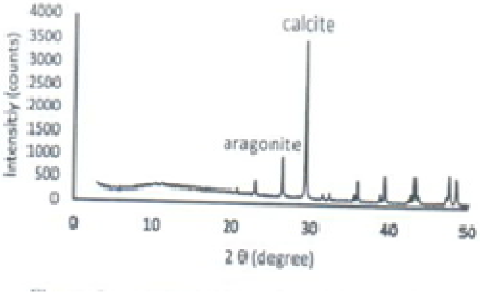

Figure 2d: XRD Pattern PWES [30].

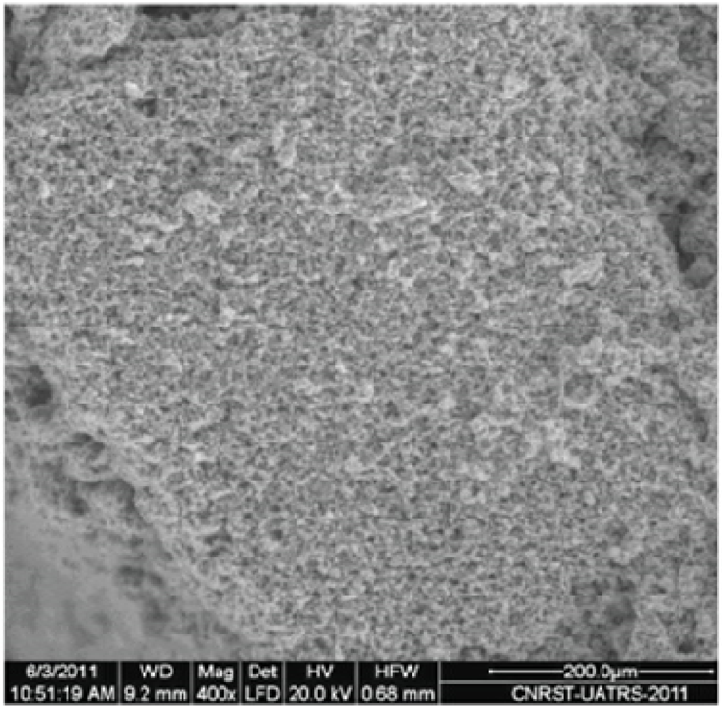

Figure 2b: Similar SEM of PWES [29].

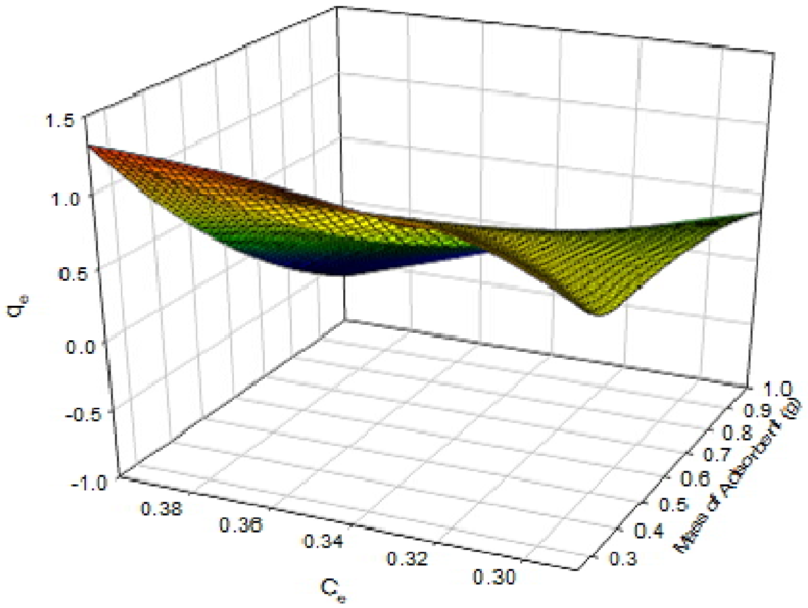

Figure 3a: Relationship between Adsorbent mass, Ce and qe synthetic AsaC

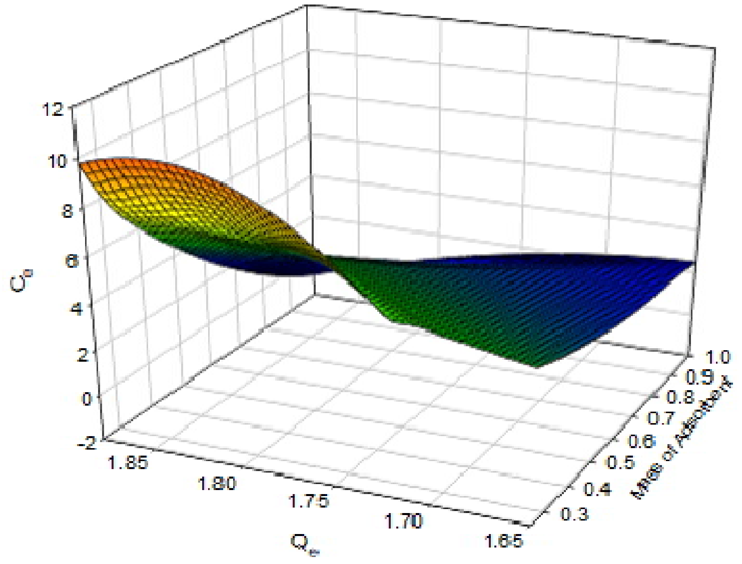

Figure 3b: Relationship between Adsorbent mass, Ce and qe raw water of AsaC

Table 1a. The thermodynamics properties of adsorption AsC from raw water samples

Factors	Values	Slope	Intercept	R^2	ΔS (J/mol.K)	ΔH (J/mol. K. h.)	ΔG (KJ/mol.K)	R
Initial Concentration (mg/l)	1.05	-10.152	12.44	0.7422	103.38	84.36	-31.24	0.862
	5.02	-5.3968	8.6765	0.6208	72.10	44.85	-21.80	0.788
	10.01	-4.4615	6.3655	0.6055	52.90	37.08	-15.99	0.778
	0.005	-12.749	14.149	0.6188	117.58	105.94	-35.52	0.787
pH	7.2	-9.1049	12.3	0.6488	102.21	75.66	-30.89	0.805
	6.4	-9.0362	12.358	0.6535	102.69	75.09	-31.04	0.808
	3.2	-8.8642	12.397	0.6496	103.02	73.66	-31.14	0.806
	11.5	-8.7139	12.439	0.6468	103.37	72.41	-31.25	0.804
Particle Size (mm,)	0.063	-10.152	12.133	0.7422	100.83	84.36	-30.47	0.862
	0.075	-8.0364	10.65	0.8805	88.50	66.78	-26.75	0.938
	0.15	-7.4928	10.162	0.815	84.45	62.27	-25.52	0.903
Mass of Adsorbent (g)	0.75	-10.152	12.44	0.7422	103.38	84.36	-31.24	0.862
	0.85	-9.1049	12.3	0.6488	102.21	75.66	-30.89	0.805
	1	-10.152	12.153	0.7472	100.99	84.36	-30.52	0.864

Table 1b The thermodynamics properties of adsorption AsC from Synthetic AsaC wastewater samples

Factors	Values	Slope	Intercept	R2	ΔS (J/mol.K)	ΔH (J/mol. K. h.)	ΔG (KJ/mol.K)	R
Initial Concentration (mg/l)	1.05	-2.2407	7.4479	0.7985	61.89	18.62	-18.73	0.894
	5.02	-2.9019	-8.1438	0.7662	-67.67	24.11	20.53	0.875
	10.01	-2.7235	8.5645	0.8534	71.17	22.63	-21.54	0.924
	0.005	-1.7086	8.8553	0.6947	73.59	14.20	-22.28	0.833
pH	7.2	-2.7235	8.4393	0.8534	70.13	22.63	-21.23	0.924
	6.4	-2.1675	7.8573	0.8738	65.29	18.01	-19.77	0.935
	3.2	-0.9836	6.5974	0.9324	54.82	8.17	-16.60	0.966
	11.5	-0.0513	5.5232	0.6868	45.90	0.43	-13.91	0.829
Particle Size (mm)	0.063	-2.2407	7.1602	0.7985	59.50	18.62	-18.01	0.894
	0.075	-3.123	8.205	0.7378	68.18	25.95	-20.63	0.859
	0.15	-2.7736	8.6398	0.3517	71.80	23.05	-21.73	0.593
Mass of Adsorbent (g)	0.75	-2.2407	7.4479	0.7985	61.89	18.62	-18.73	0.894
	0.85	-2.7235	8.4393	0.8534	70.13	22.63	-21.23	0.924
	1	-2.2407	7.1602	0.7985	59.50	18.62	-18.01	0.894

Figures 4, 5 and 6 show more data on the thermodynamic parameters. Tables 2 to 9 present results of ANOVA for the effects of the selected factors on thermodynamic adsorption of AsaC onto PWES. The study revealed that only initial concentration of AsaC had significant effects on thermodynamic adsorption of AsaC onto PWES at 95 % confidence level (Table 2). These results indicate that although, other factors had effect but these effects were not significant (Tables 3 to 9).

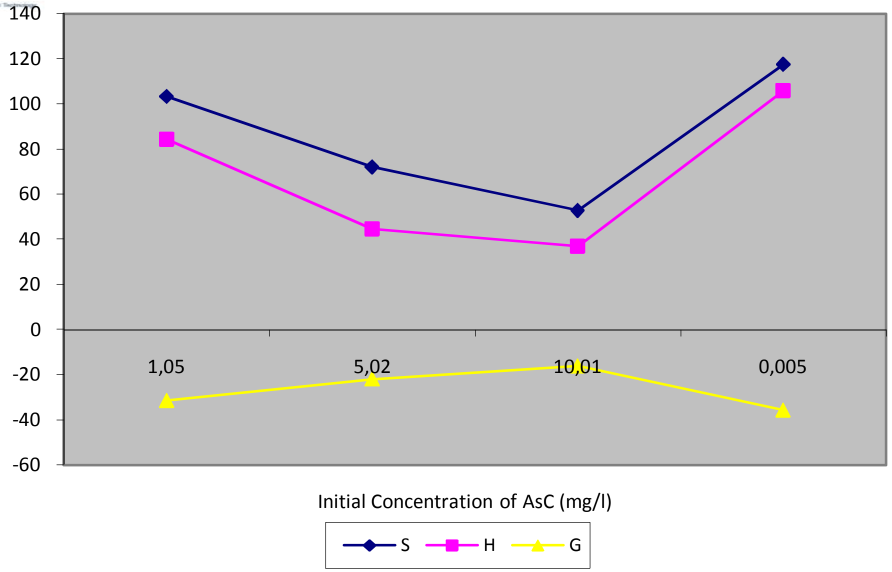

Figure 4a: Relationship between initial concentration and thermodynamic parameters

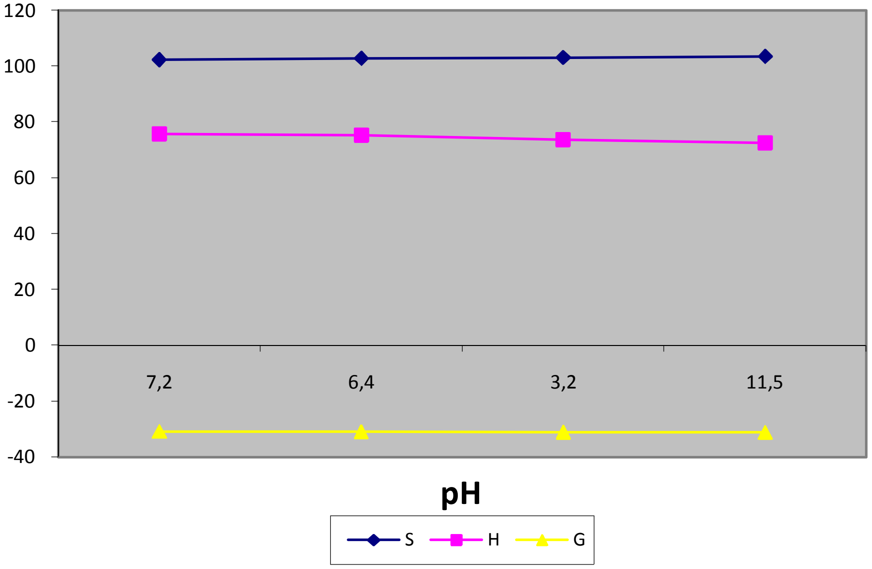

Figure 4b: Relationship between pH and thermodynamic parameters

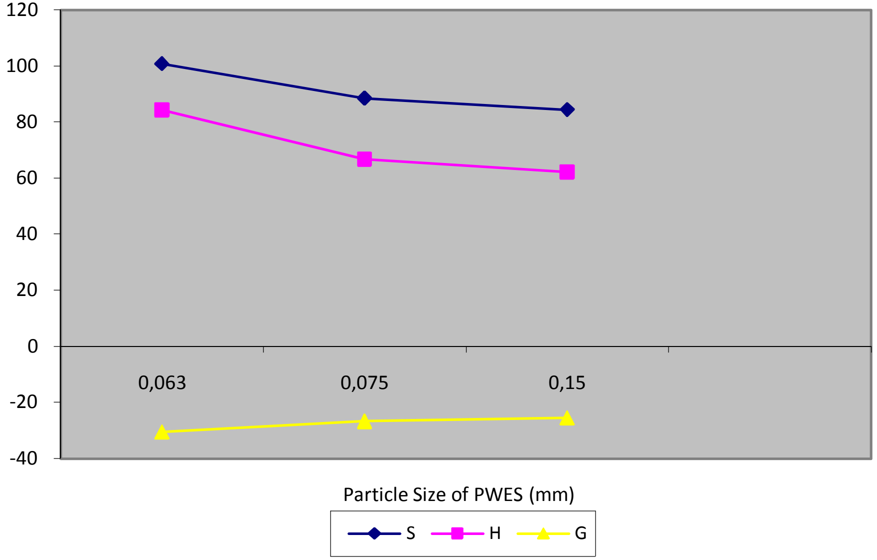

Figure 4c: Relationship between particle size and thermodynamic parameters

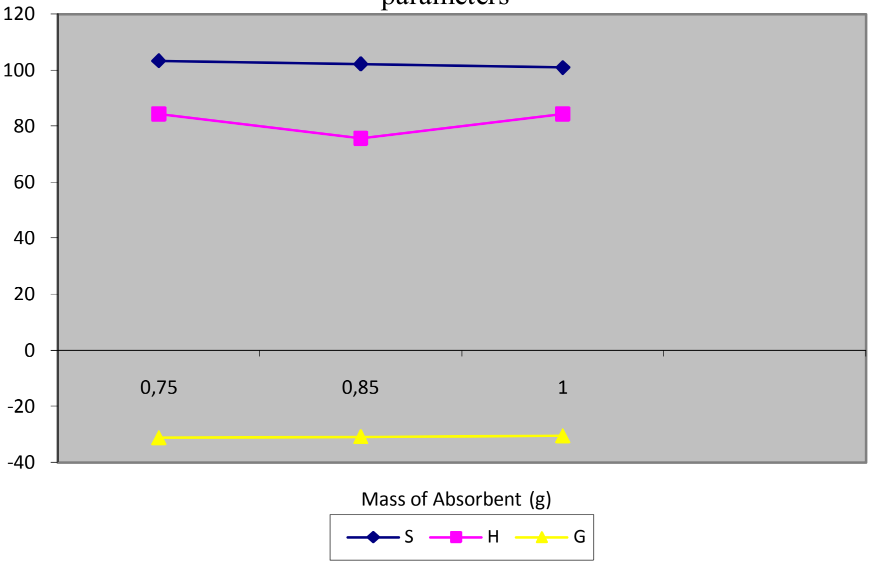

Figure 4d: Relationship between mass of adsorbent and thermodynamic parameters

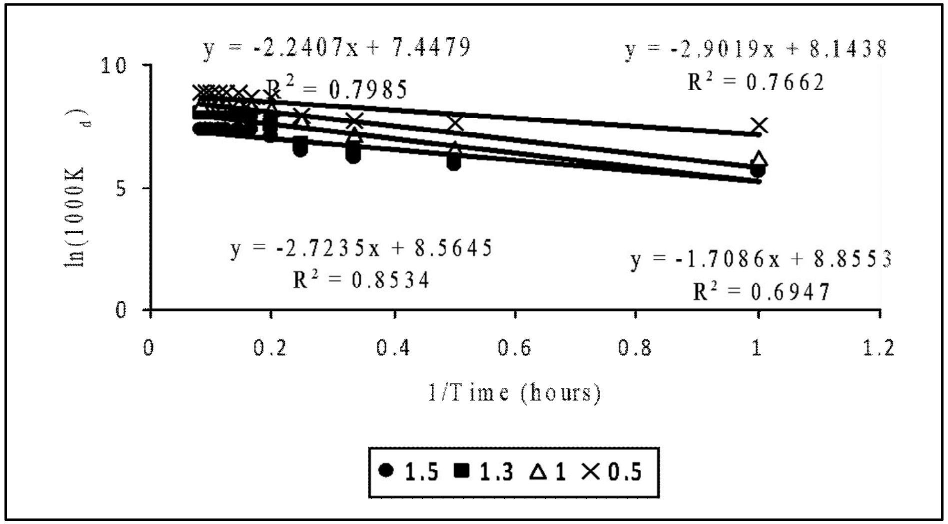

Figure 5a: Gibbs Energy of Adsorption of AsC onto PWES at various initial concentration of AsC (mg/l) in aqueous solution

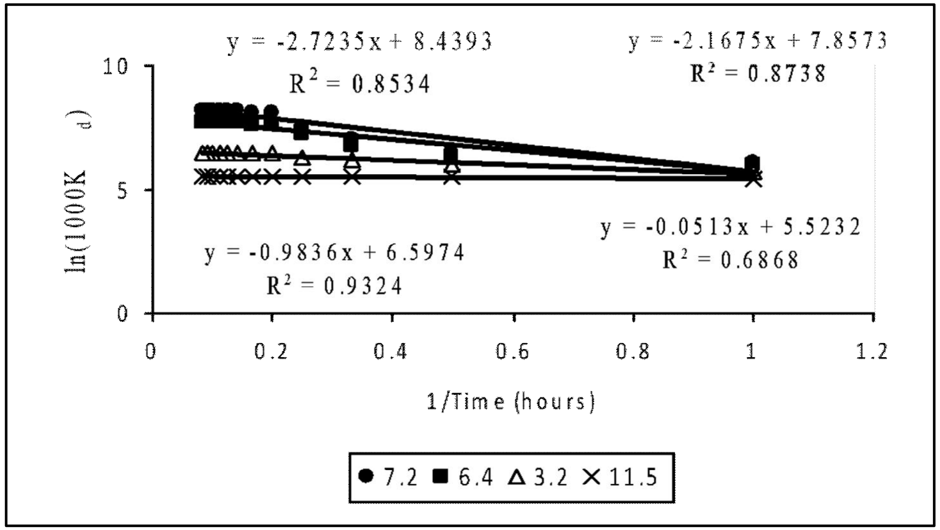

Figure 5b: Gibbs Energy of Adsorption of AsC onto PWES at various pH of aqueous solution

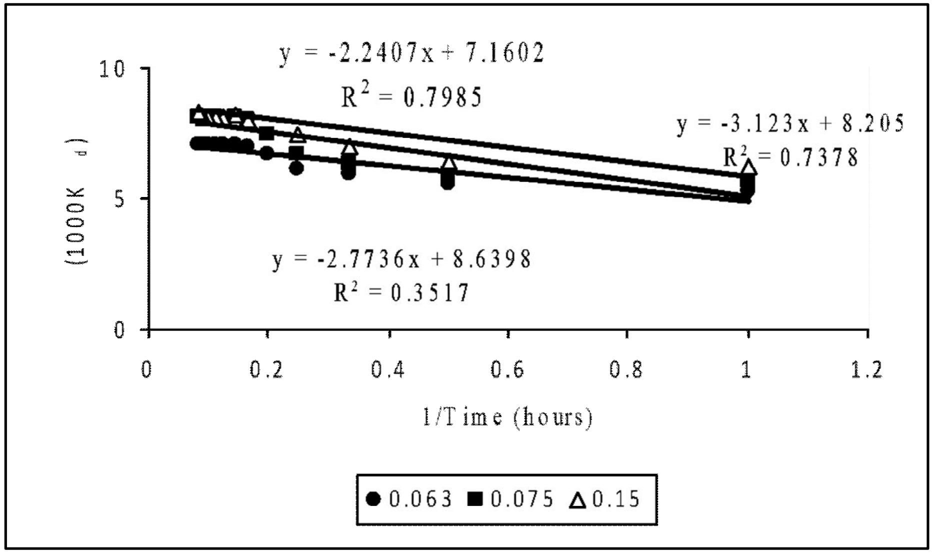

Figure 5c: Gibbs Energy of Adsorption of AsC onto PWES at various particle sizes of PWES

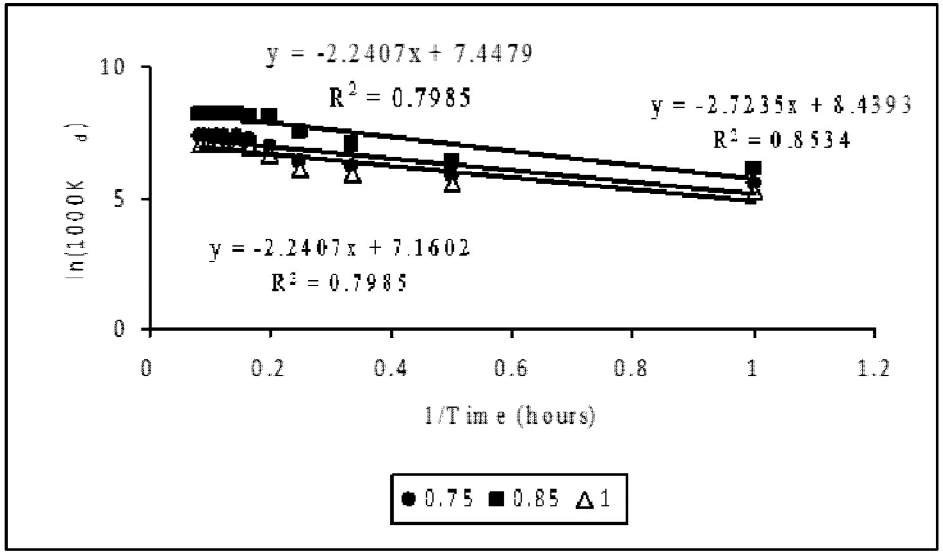

Figure 5d: Gibbs Energy of Adsorption of AsC onto PWES at various masses of PWES

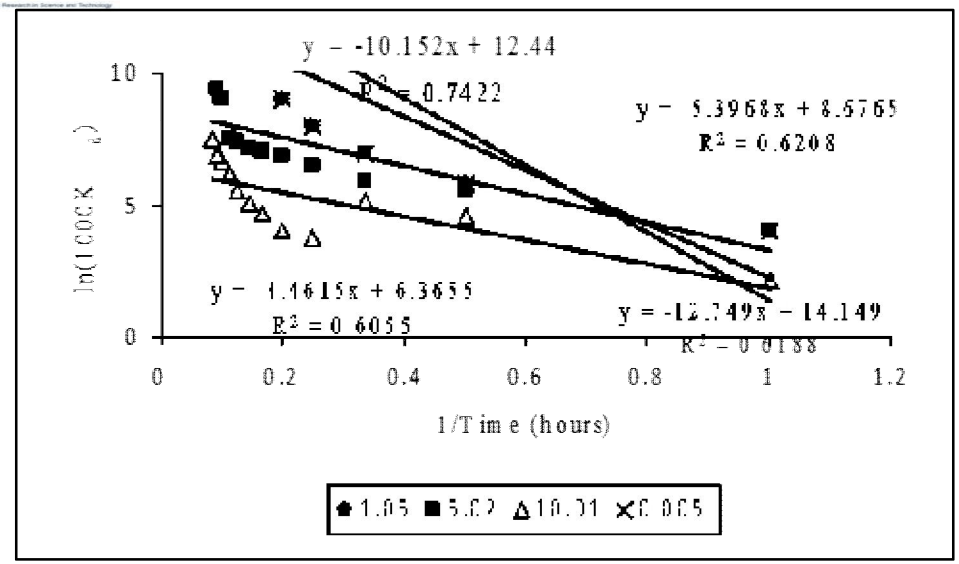

Figure 6a: Gibbs Energy of Adsorption of AsC onto PWES at various initial concentration of AsC (mg/l) in raw water

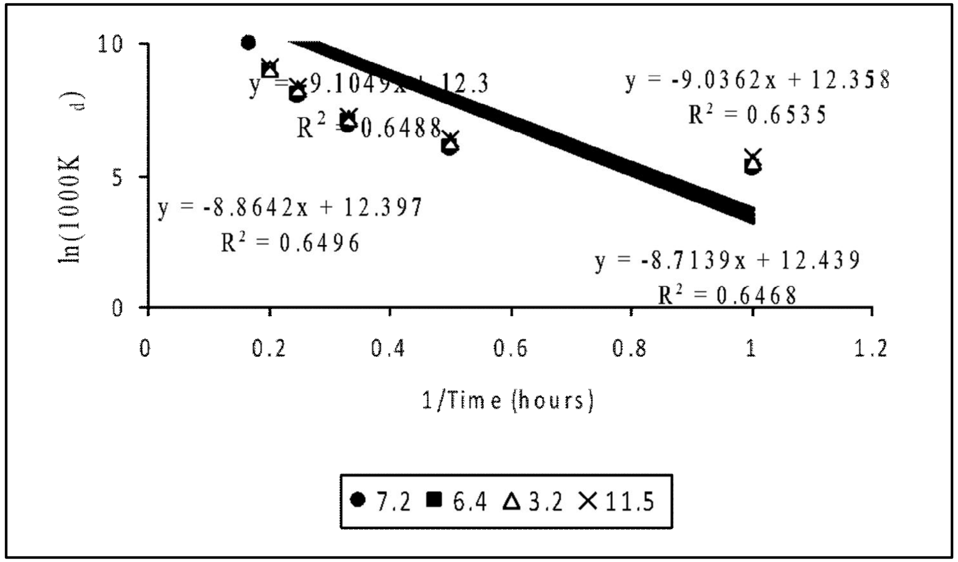

Figure 6b: Gibbs Energy of Adsorption of AsC onto PWES at various pH of raw water

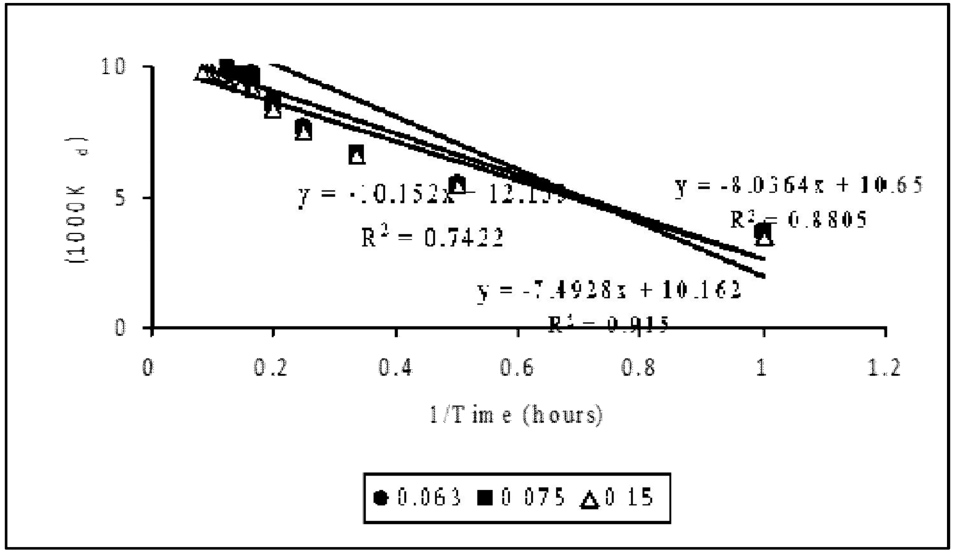

Figure 6c: Gibbs Energy of Adsorption of AsC onto PWES at various particle sizes of PWES in raw water

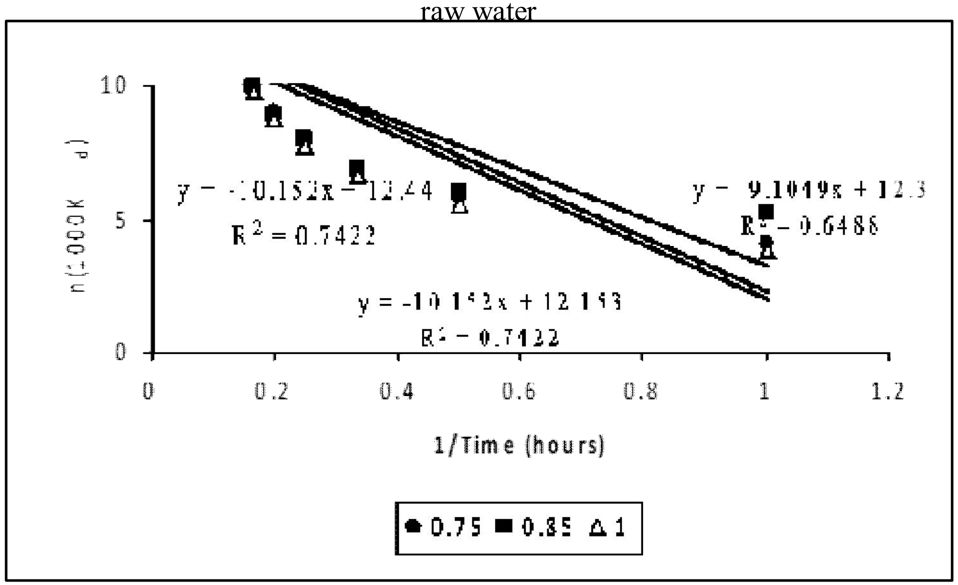

Figure 6d: Gibbs Energy of Adsorption of AsC onto PWES at various masses of PWES in raw water

Table 2: Results of effect of initial Concentration on thermodynamic synthetic AsC wastewaters

Source of Variation	*Sum of Square*	*Degree of freedom*	*Mean Sum of Square*	*F-Value*	*P-value*
Between Groups	6472.54	3	2157.51	1.07	0.46
Within Groups	8090.44	4	2022.61		
Total	14562.98	7			

Table 3: Results of effect of pH on thermodynamic of synthetic AsC Solution

Source of Variation	*Sum of Square*	*Degree of freedom*	*Mean Sum of Square*	*F-Value*	*P-value*
Between Groups	648.75	3	216.25	0.20	0.89
Within Groups	4367.82	4	1091.96		
Total	5016.57	7			

Table 4: Results of effect of Particle size on thermodynamic of synthetic AsC Solution

Source of Variation	*Sum of Square*	*Degree of freedom*	*Mean Sum of Square*	*F-Value*	*P-value*
Between Groups	89.44	2	44.72	0.05	0.96
Within Groups	2915.57	3	971.86		
Total	3005.01	5			

Table 5: : Results of effect of mass of adsorbent on thermodynamic of synthetic AsC Solution

Source of Variation	*Sum of Square*	*Degree of freedom*	*Mean Sum of Square*	*F-Value*	*P-value*
Between Groups	61.6939	2	30.84695	0.031912	0.968916
Within Groups	2899.9	3	966.6333		
Total	2961.594	5			

Table 6 : Results of effect of initial Concentration on thermodynamic Raw water

Source of Variation	*Sum of Square*	*Degree of freedom*	*Mean Sum of Square*	*F-Value*	*P-value*
Between Groups	5721.415	3	1907.138	10.2397	0.02391
Within Groups	744.9977	4	186.2494		
Total	6466.412	7			

Table 7 Results of effect of pH on thermodynamic Raw water

Source of Variation	*Sum of Square*	*Degree of freedom*	*Mean Sum of Square*	*F-Value*	*P-value*
Between Groups	1.483944	3	0.494648	0.001204	0.999932
Within Groups	1643.537	4	410.8844		
Total	1645.021	7			

Table 8 Results of effect of Particle size on thermodynamic Raw water

Source of Variation	*Sum of Square*	*Degree of freedom*	*Mean Sum of Square*	*F-Value*	*P-value*
Between Groups	408.0395	2	204.0198	0.991417	0.467162
Within Groups	617.3579	3	205.786		
Total	1025.397	5			

Table 9 : Results of effect of mass of adsorbent on thermodynamic Raw water

Source of Variation	*Sum of Square*	*Degree of freedom*	*Mean Sum of Square*	*F-Value*	*P-value*
etween Groups	26.49171	2	13.24585	0.059178	0.943611
Within Groups	671.488	3	223.8293		
Total	697.9797	5			

Figure 4 (a, b, and d) shows that initial concentration of AsC, pH, particle size of PWES and mass of adsorbent were negative factors to thermodynamics properties such as ΔS° and ΔH°, which indicated that as initial concentration of AsC increased these two thermodynamic parameters decreased. It is obvious that the thermodynamics of adsorption for AsC decreased with time and initial concentration (Figures 5 and 6) indicating that PWES is heterogeneous adsorbent [26]. These actions can be attributed to lower movement of the particle as well higher collision factors between these particles during the mobility. In addition, for ΔG° these selected operational factors (pH, initial Concentration of AsC, particle size of PWES and mass of the absorbent) are positive factors, which indicated that as these selected operational factors increased, ΔG° increased. All these can be attributed to several reaction factors such as increase in H+(increase in pH), which increased repulsive forces between H+ and AsC ions thus promote more free energy. Increase in mass of the adsorbent increase the number and available Ca2+, Fe2+, Al3+ and other cations present in PWES, thus increased repulsive forces. Increased in the particle size reduced in the available surface area PWES thus increased the number of available cations and collision forces. That is, with low adsorption capacities, AsC occupied the most energetically favorable sites, dominated by adsorbent–adsorbate (PWES- AsC) interactions, while with higher adsorption capacities, multilayers adsorption occurred and the less energetic PWES- AsC interactions play a major role. Tables 2 and 6 present effect of initial concentration of AsC on both synthetic AsC wastewater and raw water, respectively. These tables revealed that this operational factor had effect on thermodynamics of AsC adsorption kinetics but the effects were not significant at 95 % confidence level for synthetic AsC wastewater ($F_{3,4} = 1.07$; $p = 0.46$) and significant for raw water ($F_{3,4} = 10.24$; $p = 0.02$). Tables 3 and 7 present effect of pH of the solution on both synthetic AsC wastewater and raw water, respectively. These tables revealed that this operational factor had effect on thermodynamics of AsC adsorption kinetics but the effects were not significant at 95 % confidence level for both synthetic AsC wastewater ($F_{3,4} = 0.20$; $p = 0.89$) and raw water ($F_{3,4} = 0.0012$; $p = 0.9999$).

Tables 4 and 8 present effect of particle size of the PWES on both synthetic AsC wastewater and raw water, respectively. These tables revealed that this operational factor had effect on thermodynamics of AsC adsorption kinetics but the effects were not significant at 95 % confidence level for both synthetic AsC wastewater ($F_{3,4} = 0.050$; $p = 0.96$) and raw water ($F_{3,4} = 0.991$; $p = 0.467$). Tables 5 and 9 present effect of mass of the adsorbent on both synthetic AsC wastewater and raw water, respectively. These tables revealed that this operational factor had effect on thermodynamics of AsC adsorption kinetics but the effects were not significant at 95 % confidence level for both synthetic AsC wastewater ($F_{3,4} = 0.032$; $p = 0.969$) and raw water ($F_{3,4} = 0.059$; $p = 0.944$).

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4. Conclusion

This study evaluated performance of PWES in removing AsaC from both synthetic and raw water. Mechanism and thermodynamic were studied. It can be concluded based on the findings that
AsaCcan be removed by PWES (an inexpensive waste product),
PWES contains Ca, Al, and Fe, which aided in AsaC removal from water and wastewaters,
Thermodynamic studies with modified Van'tHott's equation revealed that the adsorption process was endothermic and PWES has strong affinity for AsaC

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