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Full Length Research Article

REMOVAL OF PHARMACEUTICAL COMPOUND (IBUPROFEN) USING A NOVEL MODIFIED POLYACRYLONITRILE GRAFTED PALM SEED POWDER

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ABSTRACT
Adsorption of ibuprofen onto a low cost amidoxime-modified poly(AN-*g*-PSP) has been investigated. Poly(acrylonitrile-grafted-palm seed powder) (poly(AN-*g*-PSP)) was chemically modified with hydroxylamine hydrochloride ($NH_2OH.HCl$) to convert the nitrile groups into oxime functional groups. The PSP and amidoxime-modified poly(AN-*g*-PSP) were characterized by Brauner-Emmet-Teller (BET). It was observed that the specific surface area, pore volume and average pore diameter of were significantly increased after modification with $NH_2OH.HCl$. The influence of pH, contact time, adsorbent dosage and initial metal concentration towards the adsorption of ibuprofen onto amidoxime-modified poly(AN-g-PSP) were carried out via HPLC coupled with UV. The adsorption kinetic study showed that the maximum time required for the removal of ibuprofen to reach equilibrium was found to be 40 min., at pH 6.0 , adsorbent dose 0.30 g with initial concentration of ibuprofen of 100pm at room temperature.

Keywords: Adsorption, pharmaceutical compound, polyacrylonitrile, palm seed powder

1. INTRODUCTION
Pharmaceutical compounds and personal care products (PPCPs) residues are environmental micro contaminants that received lack of attention until the late 1990s. In addition, the availability of sophisticated analytical instrumentation and methodologies capable of detecting the ultra-trace quantities of PPCPs are not widely reported (Ternes *et al.,* 2001, Al-Qaim *et al.,* 2014). This is due to lack of sensitive analytical methods to detect low concentrations of pharmaceuticals in the environment (Al-Qaim *et al.,* 2014). PPCPs may enter the aquatic environment due to the veterinary medicines usage *via* medicated fish feed and agricultural soil leaching (Boxall *et al*., 2004), industrial activities (Buchberger *et al.,* 2007) or human waste disposal to wastewater treatment plants; where they may totally biodegrade, partially biodegrade or persist (Matongo *et al.,* 2015). Pharmaceutical residues have many physiochemicals and biological properties that must be considered to predict their fate in the environment (McEneff *et al.,* 2014). Pharmaceuticals are polar compounds and biologically active at low concentrations. The toxicity studies of pharmaceuticals at relevant concentrations towards non-target aquatic species have been reported previously (Boxall *et al*., 2004, Huerta *et al*. 2012, Quinn *et al*. 2011, Schmidt *et al*., 2011). The trace of pharmaceuticals were detected in drinking water (Benotti *et al*., 2009) and in cooked seafood (Uno *et al*., 2010) that may potentially risk the safety of consumer either through direct effect or indirectly through potential antimicrobial resistance (Cabello *et al*., 2006). There is a risk for acute and chronic effects in the environment inherent to the release of pharmaceutical residues in water as some of the drugs cause endocrine disruption that is deleterious for the entire aquatic ecosystem. Pharmaceuticals exist in low concentrations in the environment (down to few nanograms per liter. Hence, there is a requirement to develop more sensitive analytical methods to enhance the detection of pharmaceutical residues (Fatta-Kassinos *et al.,* 2011, Boiussou-Schurtz *et al*., 2014). In current research, our approach is to improve the adsorption of palm seed powder, by introducing a modifier that will adsorb the pharmaceutical compound (ibuprofen) more effectively, using hydroxylamine hydrochloride.

2.0 MATERIALS AND METHODS

2.1 Chemicals
All the chemicals used in this research were of analytical grade. The pharmaceutical drug used (ibuprofen) was purchased from (Merck Co., United Kingdom, 99%). The solution of the drug was prepared using deionized water. The palm seeds (PS) were bought locally in one of the Nigerian market and acrylonitrile was purchased from (Merck Co., United Kingdom, 99%). Aluminium Oxide (Al_2O_3) (Merck Co., Germany) was used to purification of acrylonitrile. Potassium persulphate (KPS) (Systerm Chemical, Malaysia, analytical reagent) and sodium persulfate (SPS) (Systerm Chemical, Malaysia, analytical reagent).

2.2 Preparation of palm seeds powder
The prepare of palm seeds, synthesis of poly(AN-g-PSP) and chemical modification of The amidoxime-modified poly(AN-*g*-PSP) were all carried out in our previous articles (Jamil *et al.,* 2015).

2.3 Characterization of the modified and un-modified adsorbent

2.3.1 Surface area and porosity analysis
Surface area and porosity are among the most important characteristics of solid materials that determine their properties such as thermal conductivity, thermal diffusivity and diffusion coefficient. In order to determine the surface areas and pore characteristics of various polymer samples, nitrogen adsorption-desorption isotherms were monitored at 77.3 K on automatic instrument (Model 1994-2008 version 2.01, USA). Prior to measurement, all the polymer samples were degassed at 300 °C under the nitrogen flow for at least 12 h. The data analysis was based on the adsorption-desorption isother

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2.4 Batch scale adsorption

Batch experiment was performed at room temperature (25°C) in order to establish the sorption capacity towards the removal of ibuprofen drug by mixing the sorbent with 100 mL of solution in a 250 mL conical flask. The mixture was magnetically stirred at 200 rpm for 2 h. 5 mL was withdrawn from the bulk solution and filtered using membranes filter. The initial and final concentration of metal ions was then analysed using HPLC embedded with a UV detector. The percentage removal of the MB was computed using the following equation.

$$Removal\ efficiency = (C_o - C_e)/C_o\ x\ 100 \quad (1)$$

where C_o and C_e are the initial and the equilibrium concentrations (mg.L^{-1}) respectively. The adsorption capacity at equilibrium q_e (mg.g^{-1}) was calculated using equation (2).

$$q_e = \frac{C_o - C_e}{m} x\ V \quad (2)$$

where V corresponds to volume of the aqueous phase and m is the mass of the adsorbate (mg).

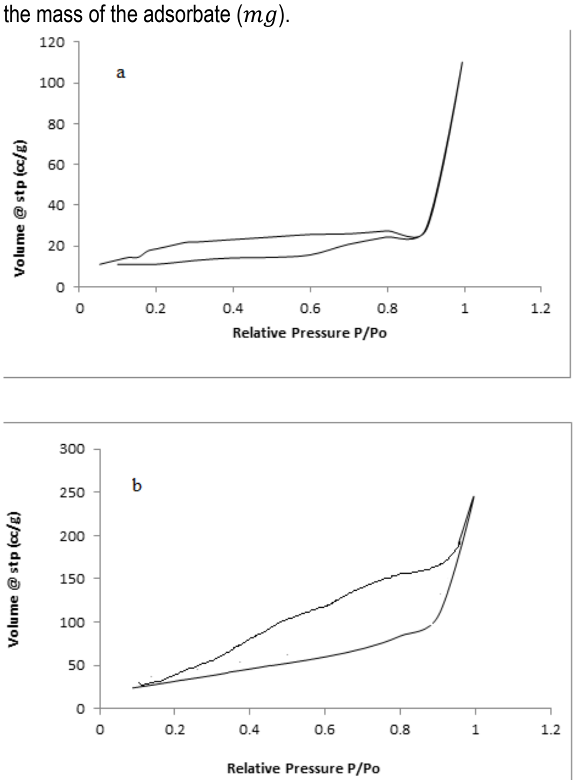

Figure 1. Adsorption isotherm of nitrogen at 77 k of (a) PSP (b) amodified poly(AN-*g*-PSP)

Table 1: Textural characteristics of un-modified PSP and modified poly(AN-*g*-PSP)

Sample	Analysis gas	Outgas Temp(°C)	Sample weight (g)	Molecular weight (g)	Mesopore volume ($cm^3 g^{-1}$)	$S_{BET} (cm^3 g^{-1})$
PSP	Nitrogen	110	0.0215	28.0134	0.410	64.75
Amodified poly(AN-*g*-PSP)	Nitrogen	110	0.0123	28.0134	0.820	135.40

3.2 Adsorption Studies

3.2.1 Effect of Contact Time on ibuprofen Adsorption

The removal of ibuprofen drug was investigated at varying contact time. The ibuprofen adsorption onto amidoxime-modified poly(AN-*g*-PSP) was found to occur within 40 min. and equilibrium was reached at about 50 min. ibuprofen drug removal by amidoxime-modified poly(AN-*g*-PSP) from aqueous solution proceeds in a rapid manner at the early stage (10 – 40 min.) of adsorption and this could be due to high number of free available adsorption sites and after about 40 min, a decreasing removal percent was observed resulting from saturation of the active sites until equilibrium was attained at 40 min as shown in (Fig. 2). After equilibrium was achieved no feasible uptake was further observed (Baek *et al.,* 2010).

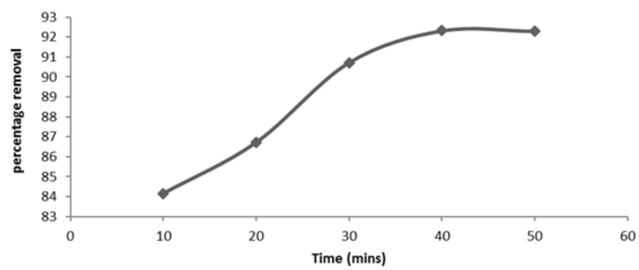

Figure 2: Effect of contact time on the sorption capacity of ibuprofen drug onto amidoxime-modified poly(AN-*g*-PSP) (Adsorbent dosage 0.3 g: volume of the ibuprofen drug solution: 50 ml, initial concentration of ibuprofen drug 100 ppm, pH: 6.0, temperature: 298 K, particle size: 75-300 µm)

Table 2. Contact time study data for ibuprofen drug removal using amidoxime-modified poly(AN-*g*-PSP)

Time (mins)	Adsorbance	C_e(mg/L)	Q_e (mg/g)	Removal %
10	0.780	7.72	15.38	92.28
20	0.653	6.46	15.59	93.54
30	0.457	4.52	15.92	95.48
40	0.385	3.81	16.03	96.19
50	0.854	3.80	16.03	96.20

3.2.2 Effect of pH on ibuprofen drug Adsorption

The pH is a significant factor affecting adsorption of pollutants from wastewater. Adsorption of ibuprofen drug onto amidoxime-modified poly(AN-*g*-PSP) was found to increase with increasing pH from 2 - 7, and the maximum uptake capacity was attained at pH 6. These phenomena may be ascribed to the electrostatic interaction between cationic ibuprofen drug and the negative surface of the amidoxime-modified poly(AN-*g*-PSP). At low pH range the surfaces of PSP were protonated and competition set in between the amidoxime-modified poly(AN-*g*-PSP) surfaces and ibuprofen drug resulting in low uptake capacity as shown in (Fig. 3).

As the solution pH increases, a decreasing charge density on the PSP surfaces was obtained, which is favorable for electrostatic interaction with cationic pollutants. At pH above 7.0, no substantial uptake was observed and this could be as a result of saturation of the actives site or low stability of the dye molecules at higher pH as

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reported elsewhere (Gecgel *et al*., 2013).

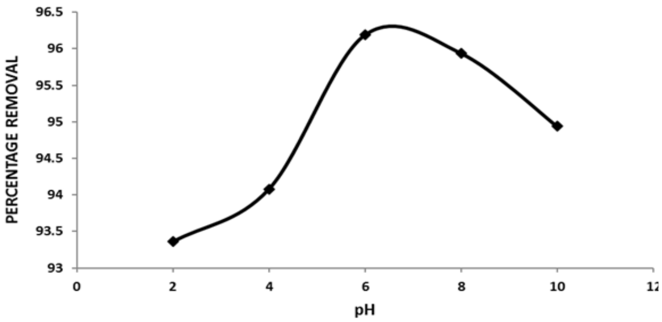

Figure 3: Effect of initial drug solution pH on the sorption of ibuprofen drug capacity onto amidoxime-modified poly(AN-*g*-PSP) (Adsorbent dosage: 0.3g, Volume of the ibuprofen drug solution: 50 ml, Temperature: 298 K, initial concentration of ibuprofen drug 100 ppm, pH: 2, 4, 6, 7, 8 and 10, Particle size: 75-300 µm, Agitation speed: 200 rpm).

Table 3: Effect of pH and % removal of ibuprofen drug using amidoxime-modified poly(AN-*g*-PSP)

pH	Adsorbance	C_e(mg/L)	Q_e (mg/g)	% removal
2	0.671	6.64	15.56	93.36
4	0.599	5.92	15.68	94.08
6	0.385	3.81	16.03	96.19
8	0.452	4.48	15.92	95.52
10	0.512	5.07	15.83	94.94

3.2.3 Effect of Initial Concentration on ibuprofen drug Adsorption

The effect of initial concentration of ibuprofen drug as a function of contact time is shown in (Figure 4). The amount of ibuprofen drug adsorbed decreases with increase in initial concentration, while maximum adsorption was obtained at lower concentration. The highest amount of ibuprofen drug adsorbed onto amidoxime-modified poly(AN-*g*-PSP) was attained at about 40 mins which is an indication that the adsorption is relatively fast due to the presence of more adsorption sites. At higher ibuprofen drug concentration, lower uptake capacity could be as a result of high ratio of drug molecules available sites and fractional adsorption subsequently becomes dependent on initial concentration. Thus, Fractional adsorption becomes independent on the initial concentration in the case of lower concentrations where the ratio of initial number of drug moles to the free available binding sites is low (Ayla *et al.,* 2013).

Table 4: Percentage removal of ibuprofen drug at different concentrations

Conc. (ppm)	Adsorbance	C_e(mg/L)	Q_e (mg/g)	% removal
25	0.125	1.23	3.96	95.0
50	0.295	2.92	7.85	94.16
75	0.496	4.91	11.68	93.45
100	0.383	3.79	16.04	96.21

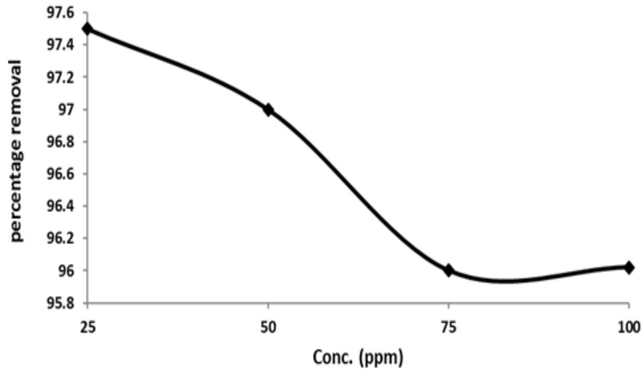

Figure 4: The effect of the initial ibuprofen drug concentration onto amidoxime-modified poly(AN-*g*-PSP) (Adsorbent dosage: 0.3 g, volume of the ibuprofen drug solution: 50 ml, pH: 6.0, temperature: 298 K, particle size: 75-300 µm, agitation speeds: 200 rpm)

3.2.4 The Effect of adsorbent Dosage on ibuprofen drug

The removal percent was observed to increase with increasing adsorbent dosages due increased surface area and active functional groups, resulting in increased removal efficiency of the removal of ibuprofen drug. Meanwhile, an opposite trend was observed with the uptake capacities shown in (Figure 5). A decreasing uptake capacity with increasing amidoxime-modified poly(AN-*g*-PSP) dosage could be as a result of rapid saturation of the total adsorption sites as the treatment process proceed and similar observation have been reported elsewhere (Baek *et al.,* 2010).

Table 5 variation of % removal of ibuprofen drug with dosage of adsorbent

Dosage (mg)	Adsorbance	C_e(mg/L)	Q_e (mg/g)	% removal
0.1	0.703	6.95	15.50	93.05
0.2	0.512	5.06	15.83	94.94
0.3	0.385	3.78	16.03	96.22
0.4	0.381	3.77	16.03	96.23
0.5	0.382	3.78	16.03	96.23

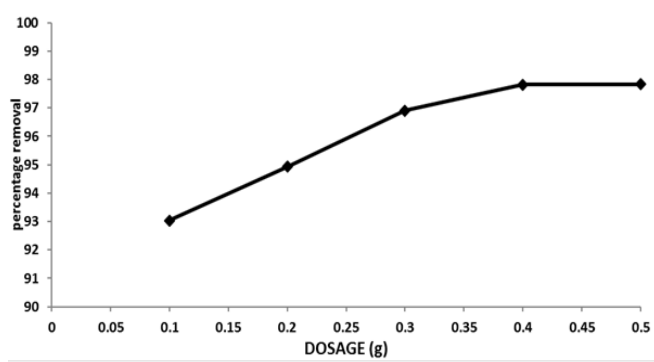

Figure 5: The effect of adsorbent dosage on ibuprofen drug concentration onto amidoxime-modified poly(AN-*g*-PSP) (volume of the ibuprofen drug solution: 50 ml, pH: 6.0, temperature: 298 K, particle size: 75-300 µm, agitation speeds: 200 rpm).

Conclusion
The synthesis of poly(AN-*g*-PSP) and its chemical modification with hydroxylamine hydrochloride to form amidoxime-modified poly(AN-*g*-PSP) were carried out in present work. The removal of ibuprofen drug using amidoxime-modified poly(AN-*g*-PSP) was used as adsorbents. Various experimental parameters were found to influence the adsorption ability of ibuprofen drug, such as, contact time, initial pH, and initial ibuprofen drug concentration. The maximum ibuprofen drug removal by all the adsorbents was observed to occur at pH 6.5. The equilibrium time was found to be 40 min. It was established that the adsorption capacity of ibuprofen drug increases as amount of dosage of the adsorbent decreases and also increase with increasing initial concentration of ibuprofen drug. The optimum removal for ibuprofen drug was recorded as 96.21%. These were achieved at a very low adsorbent dosage of 0.3 g at pH 6.

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