Uptake of p-Nitrophenol (PNP) from model aqueous solutions using raw and quaternised *Afromomum melegueta* peels

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ABSTRACT

Anthropogenic activities contribute large amounts of pollutants to the environment which threaten animal and human health. There is increased realization of the effect of these toxins on surface and ground water, consequently, their elimination is vital in rendering secure water for drinking as well as culpable release of effluents to our habitats. Phenolic compounds cause serious health effects to both humans and animals; a *p*-Nitrophenol concentration of 1 ppb changes the taste and odour of water as well as meat and fish quality. In humans, exposure to PNP causes eye and skin burns while its interaction with blood leads to confusion, cyanosis and unconsciousness. It is imperative therefore to find ways for removing PNP from water. Among the available techniques for removing PNP from water, adsorption is more convenient and offers more advantages because of its design, simplicity, and operating flexibility. The present study involved application of peels of raw *Afromomum melegueta* (RAM) and quaternised *Afromomum melegueta* (QAM) to remove PNP from water through adsorption. The raw adsorbents were modified with a quaternary ammonium salt to improve their uptake efficiency. The impact of experimental parameters; contact time, pH, sorbent dose, temperature and concentration were investigated. Attenuated FTIR technique was employed to characterize the adsorbent materials. It was established that the quaternary ammonium compound was anchored chemically within the cellulose structure of *Afromomum melegueta* peels. The behavior of adsorption of PNP was investigated using Langmuir and Freundlich isotherm models. The physical sorption load was 8.70 and 106.38 mg/g for RAM and QAM peels respectively from Langmuir adsorption equation. Uptake of PNP is high at

the first 30 mins of contact and at sorbent dosage of 0.01 g and 0.03 g for RAM and QAM respectively. Quantity of PNP removed increases as the initial concentration rises however, adsorption decreases after a concentration exceeding 30 mg/L. The ideal pH and temperature for PNP removal is at pH 3 and 25 °C respectively. In conclusion, the findings suggest that *Afromomum melegueta* peels can be friendly to the environment, cheap biosorbents and efficient which can be applied for the uptake of PNP from drinking water

Key Words: *Afromomum melegueta*, Adsorption, quaternised, *p*-Nitrophenol, Isotherms

INTRODUCTION

Phenolic compounds contain one or more hydroxyl group directly bonded to a benzene ring (Mwangi et al., 2014). These compounds dissociate easily in aqueous solution and are more acidic than corresponding alcohols since the O-H bond is weak in phenols as a result of a pool of mobile electrons that causes the ring to be stable by withdrawal of electron by the different ring substituents (Crisponi et al., 2002). Further, phenolic compounds exhibit different properties due to the presence of different bonded substituents as well as other functional groups (Crisponi et al., 2002). Dissolution of most phenolic compounds yields the corresponding phenolate ion, with the insoluble phenolic compounds disintegrating to give simpler water soluble phenolic compounds which can eventually find their way into various water bodies and cause pollution (Mwangi et al., 2014).

Dissolution of PNP in water yields an aqueous solution that is slightly acidic. Consequently, PNP is a central chemical compound in a host of industrial processes which include: pesticide, petrochemical, pharmaceutical, dyes and paints, oil refineries, plastics, pulp and paper mill, hence effluents generated from such industries will contain PNP (Ahmad et al., 2011). The effluents containing PNP will then be deposited in soil and water thus causing pollution (Parida & Prakasini, 2004). ATSDR (1992) reported that PNP is an eye irritant while on ingestion or inhalation brings about vomiting, sleepiness, headaches, and ataxia. Recently PNP was reported by US Environmental Protection Agency to be one of the most poisonous, bioaccumulative and indestructible organic compound which causes adverse effects to humans and animals even at negligible concentrations (Abdel-Ghani et al., 2016).

In view of the environmental impacts of PNP on humans and animals, appreciable research work has been done aimed at effective removal of PNP or the reduction of its concentration from aqueous media. It is therefore imperative to develop cheaper methods for removing PNP from water to the developing communities through preparation of alternative adsorbents from locally available materials and which are renewable. Among the materials that has not been exploited for water remediation is *Afromomum melegueta*. This plant is herbaceous and grows in swampy habitats, its fruits are purple and are trumpet-shaped with many small, reddish-brown aromatic seeds (Ilic et al., 2010). In Kenya, the fruit is abundant in Chogoria, Tharaka-Nithi County and other parts of Meru County. In the present study, the peels of this fruit were utilized in their raw and modified forms for the uptake of PNP from water.

MATERIAL AND METHODS

Chemicals, reagents and solvents

The reagents used were of analytical grade and all the solutions were prepared in distilled-deionized water at chemistry laboratory of Kenyatta University in Nairobi, Kenya. The phenolic compound used was *p*-Nitrophenol (PNP). Other reagents included: propylene oxide, epichlorohydrin, polyDADMAC, sodium hydroxide, hydrochloric acid, ammonium acetate and methanol. Stock solutions of 1000 µg/L concentration of PNP were prepared in ammonium acetate buffer solution from which working solutions were obtained. The pH of working solutions was adjusted with either 0.1 M sodium hydroxide or 0.1 M hydrochloric acid.

Preparation of the quaternised adsorbents

The *Afromomum melegueta* peels were collected locally and were transported to the laboratories, washed thoroughly

with deionized water to purify them, then chopped into pieces before they were oven dried at 105 °C to eliminate moisture. The adsorbents were ground into powder and sieved. The resulting solids were labeled and kept in desiccators until used. The ground adsorbents were then chemically modified using method described by Mwangi et al. (2014). The dry powder of *Afromomum melegueta* peels was activated for 12 hrs; 280 g of this sample was transferred into a two litre three necked flask after which 420 cm³ of 0.625 M NaOH was added. A solution made by dissolving 16.8 cm³ of epichlorohydrin in 140 cm³ of propylene oxide was introduced into the flask contents. Thorough stirring of the mixture was done until all the liquid had dried and there was no more enlargement of the material. This reaction was carried out at a temperature of 25 °C and gradually raising it to 50 °C for 1 hour in a thermostatic water bath. Epoxidation procedure followed is coherent with the one used by Bortolini et al. (2002). A mixture of 40 g solid sample of hydroxypropylated *Afromomum melegueta* peels and the epoxidated polyDADMAC at 4 °C were placed in a 500 cm³ three neck flask after which 2.8 g of sodium hydroxide was added and the mixture agitated intensively for 30 mins. The agitation continued for further 6 hours at 60 °C while maintaining the pH above 8 (Bortolini et al., 2002). Finally, the mixture was filtered by vacuum filtration to obtain the residue which was washed using distilled water to lower the pH to 7. The modified adsorbent material was air dried. The two adsorbents; the raw *Afromomum melegueta* (RAM) and quaternised *Afromomum melegueta* (QAM) were later characterized using FTIR.

Instrumentation

The raw and quaternised adsorbents were characterized using a Shimadzu Fourier transform infrared (FTIR-IR tracer-200) spectrophotometer to identify the functional groups contained in the raw and modified adsorbents (Han et al., 2010). The PNP concentration in water was obtained using a double beam UV-Vis spectrophotometer (Model Specord 200, Analytik Jena) at maximum solution wavelength of 318 nm.

Optimization of adsorption parameters

Influence of parameters: contact time, pH, initial PNP concentration, amount of sorbent and temperature on uptake efficiency of the raw and quaternised sorbents was done by maintaining other parameters stable while changing the one under investigation (Mwangi & Ngila, 2012). Variation of process parameters was done as follows; solution pH (3 - 9), contact time (1 - 150 min), sorbent dose (0.01 - 0.06 g), initial PNP concentration (5 - 100 mg/L) and temperature (15-90° C) in 20 mL aqueous solution.

RESULTS AND DISCUSSION

FTIR characterisation

The results from FTIR spectrum of RAM and QAM indicated the presence of a narrow band at 3425.58 cm^{-1} , this is characteristic of the existence of stretching vibrations of -OH or -NH groups (Stuart, 1996) while the signal at 2924.09 cm^{-1} in RAM and QAM are attributed to -CH stretches and hydroxyl group in a carboxylic acid. The signal at 1458 cm^{-1} was assigned to -OH stretches in carboxylic acids while the peak at 1110 cm^{-1} was assigned to an organic siloxane or silicone. Absorbance at 2276 cm^{-1} in QAM was assigned to isocyanate stretch while the peak at 1373.32 cm^{-1} in QAM was assigned to aliphatic nitro compounds. The signal at 1265.30 cm^{-1} in QAM could be due to aromatic ethers or aryl-O stretch functional group. The peak at 1458 cm^{-1} in RAM was allocated to -OH stretch in carboxylic acids while the peak at 1064.71 cm^{-1} was assigned to primary amine -NH stretch. The band at 1519.91 cm^{-1} can be attributed to an aromatic ring of lignin in the RAM; this band disappears in the QAM suggesting a reaction of depolymerization of aromatic ring of lignin that could have led to removal of lignin (Merkel et al., 2014). In QAM the appearance of the peak at 2345.44 cm^{-1} after modification is attributed to an amine group, -NH_4^+ or its derivatives. The band at 1651.36 cm^{-1} moved to 1627.92 cm^{-1} owing to NH_2 deformation of amines, the signal at 1458.18 cm^{-1} in RAM relocated to 1435.04 cm^{-1} (Pavia et al., 1996). The FTIR spectra for the raw and quaternised adsorbents is presented in Figure 1.

Figure 1. FTIR spectra of (A) raw *Afromomum melegueta* (RAM) peels and (B) quaternised *Afromomum melegueta* (QAM) peels

Influence of pH on adsorption of PNP

Batches of 0.03 g of the raw and quaternised adsorbents were separately weighed into screw cap bottles containing 20 mL of the model solution containing 30 mg/L and adjusting the pH of the solution to the desired values of between 3 and 9 using 0.1 M HCl or 0.1 M NaOH. These mixtures were then equilibrated for 60 mins after which PNP concentration was determined using UV-Vis

spectrophotometer. The results in figure 2 show the impact of pH on adsorption of PNP by raw and quaternised *Afromomum melegueta* peels (RAM and QAM). Figure 2 shows a maximum removal percentage of 88.76 % and 95.32 % for RAM and QAM respectively at pH 3. It was thus considered that pH 3 was most favorable for the adsorption of PNP onto RAM and QAM. The reduced uptake at elevated pH can be attributed to rise in dissolution of PNP and the fact that the concentration of OH ions increases thus increasing the barrier of diffusion of the negatively charged PNP ions. The adsorption of PNP can therefore be said to be favorable at low pH since in its molecular form it has its pH being lower than pKa hence the increased uptake of PNP could be as a result of the bonded -NO_2 which reduces the electron density in the aromatic ring since it's an electron withdrawing group. The results are coherent with those reported elsewhere (Mohamed et al., 2011; Asrar, 2013; Nurul et al., 2020) who established higher adsorption of PNP at lower pH.

Figure 2. Impact of pH on the adsorption of PNP on raw and quaternised *Afromomum melegueta* peels (RAM & QAM)

Impact of contact time on uptake of PNP

The influence of this parameter was investigated by having batches of 0.03 g of the raw and quaternised adsorbents weighed separately into screw cap bottles containing 20 mL of the model solution containing 30 mg/L and adjusting the pH of the solution to the desired value. Contact time intervals applied were: 1, 10, 30, 50, 70, 90, 110, 130 and 150 mins. Uptake of PNP was influenced by adsorbate residence time as shown in figure 3, the rate of uptake was rapid during first 45 minutes in the raw and quaternised *Afromomum melegueta* peels. However, maximum adsorption was achieved at 30 mins in RAM peels with removal percentage of 87.42 % and 45 mins in QAM peels with removal percentage of 94.46 %. Thereafter, the rate of PNP removal approached a steady state, indicating attainment of equilibrium. At the beginning, the accelerated adsorption rate in the first 20-30 min can be attributed to physical adsorption occurring at the adsorbent surface while the decreased uptake is as

Figure 3. Impact of contact time on adsorption of PNP on raw and quaternised *Afromomum melegueta* peels (RAM & QAM)

Figure 4. Effect of sorbent dose on the adsorption of PNP on raw and quaternised *Afromomum melegueta* peels (RAM & QAM)

Figure 5. Influence of initial concentration on uptake of PNP by raw and quaternised *Afromomum melegueta* peels (RAM & QAM)

a result of other processes such as complexation (Khani, 2006). It was established that to realize maximum uptake of PNP, contact time of 30 minutes was adequate. Increase in contact time did not show any variation in concentration. Results reported are coherent with those reported by (Mohamed et al., 2011; Mwangi et al., 2014; Prashant et al., 2016; Nurul et al., 2020).

Impact of sorbent dose on uptake of p-Nitrophenol

The influence of the amount of adsorbent on uptake of PNP was evaluated by using different sorbent dose: 0.01,

0.02, 0.03, 0.04, 0.05 and 0.06 g at fixed volume of 20 mL containing 20 mg/L of PNP. The experiment was carried out at a contact time of 30 min and 45 min for RAM and QAM respectively and a solution pH of 3. Results from figure 4 shows that uptake of PNP was influenced by adsorbent dosage. Removal percentage of PNP by RAM was highest at 0.01 g and further increment in weight of sorbent made the amount of PNP removed to decrease. Uptake of PNP by QAM increased rapidly from 53.91 % at the dose of 0.01 g to 94.61 % at the dose of 0.03 g, after which it becomes almost constant. The results show that uptake of phenolate ions rises with increased sorbent doses possibly due to increase in the surface area and hence adsorption sites, this is coherent with result reported elsewhere (Asrar, 2013; Prashant et al., 2016; Nurul et al., 2020). Further increase in sorbent dose led to decreased uptake; since the sites of adsorption are laden with the sorbate besides there is solid aggregation as a result of inter particle interaction (Lataye et al., 2011). Modification improved the uptake of PNP by the adsorbent; this can be attributed to improved surface texture and micro pore structure after modification as shown in figure 5 fast-tracking the entrance of the PNP ions into sites of adsorption (Anwar et al., 2010). Since there is no increase in the adsorption beyond 0.01 g and 0.03 g for RAM and QAM, these doses were considered as the optimum adsorbent doses which were used in subsequent studies.

Influence of initial concentration on adsorption

The impact of starting concentration C_0 (5-100 mg/L) and sorbent mass of 0.01 and 0.03 g of RAM and QAM respectively on the removal of PNP at $t=30$ minutes for RAM and $t=45$ minutes for QAM at solution pH of 3 was investigated and results are shown in Figure 5. Adsorption capacity of the quaternised adsorbent was obtained by plotting the collected data as a function of PNP ion concentration adsorbed versus the initial PNP ion concentration. It was established that the amount of PNP removed rises in a linear manner and then stabilized beyond a concentration of 30 mg/L due to the fact that the fixed sorbent mass adsorbs a fixed amount of PNP at constant volume of adsorbent. The adsorbent is at this instance said to be saturated with the sorbate (Prashant et al., 2016). It was established that the uptake of PNP increases from 93.2 % to 97.1 % after modification. The percentage uptake of PNP using raw adsorbents was lower than that of modified adsorbents. Sorption of PNP from water is thus greatly favored by modification of the raw adsorbent since it makes the surface of the adsorbent to have a micro rough texture and porous. At low initial PNP concentration almost all the phenolate ions have been adsorbed from aqueous solution. As the initial PNP concentration is increased the efficiency of adsorption does not change due to the fact that the active

sites available become limited (Ilhan et al., 2004; Arshad et al., 2008; Koel et al., 2012; Mwangi and Ngila, 2012; Moyo and Chikazaza, 2013). The findings compare with those reported in the study of activated carbons in removal of PNP (Mohamed et al., 2011), adsorption of phenolic compounds from water by quaternised treated maize tassels (Mwangi et al., 2014) and application of acid treated biosorbents derived from lemon, sweet yellow passion, banana, watermelon peels and avocado seeds to adsorb heavy metals (Nthiga et al., 2016).

Impact of temperature on adsorption

The uptake of PNP from solution by the raw and modified adsorbents at temperatures: 15, 25, 35, 45, 60, 75, 90 is shown in Figure 6. Other experimental conditions were: solution pH of 3, sorbent dosage of 0.01 and 0.03 g for RAM and QAM respectively, contact times of 30 min and 45 mins for RAM and QAM respectively and initial concentration of 30 mg/L. Increase in temperature leads to decreased uptake of PNP. This could be due to the fact that increase in solution temperature leads to a rise in the solubility of PNP, hence the molecules diffusion within the adsorption sites is hindered. This is expected for physical adsorption process which in most cases is usually exothermic (Garcia et al., 2003; Li et al., 2008). It was indicated that the efficiency of adsorption was higher at 25 °C, further increase in temperature lowered the amount of PNP removed. Therefore adsorption isotherms were determined at 25 °C. Application of RAM and QAM peels for the uptake of PNP from water is thus applicable at ordinary room temperatures of 25 °C. The findings compare with those reported in the study of removal of PNP using activated carbons derived from sewage sludge (Mohamed et al., 2011).

Figure 6. Influence of temperature on the adsorption of PNP on raw and quaternised *Afromomum melegueta* peels (RAM & QAM)

Adsorption isotherms

The data on adsorption of PNP on RAM and QAM against initial concentration of PNP was fitted onto Langmuir and Freundlich isotherms which are presented in equations 1 and 2 respectively.

$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{1}{Q_{max}} C_e \quad \text{Equation 1}$$

Where C_e and q_e are initial and equilibrium PNP concentrations, q_{max} is the adsorption capacity in mg/g and b is a Langmuir constant. The values of q_{max} and b were calculated from the slope and intercept of the Langmuir isotherm equation plot of $\frac{C_e}{q_e}$ versus C_e which gives a straight line with $\frac{1}{q_{max}}$ as the intercept and $\frac{1}{bq_{max}}$ as the slope, from which q_{max} and b can be determined.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{Equation 2}$$

Where, K_f is Freundlich sorption capacity, $\frac{1}{n}$ is the adsorption intensity. For Freundlich isotherm equation, a plot of $\log q_e$ versus $\log C_e$ yields a straight line from which K_f and $\frac{1}{n}$ can be determined from the intercept and slope respectively; K_f and n are constants representing adsorption capacity and intensity respectively.

The adsorption of PNP onto QAM gave R^2 of 0.966 indicating the data fitted well in Langmuir model. The values of b of 0.2081 and 0.11648 indicate favorable adsorption process for RAM and QAM, respectively. This model prescribes a single-layered adsorption and it indicates a chemisorptions process (Deng et al., 2003; Hossain et al., 2012; Mwangi and Ngila, 2012). R^2 values gotten for RAM show that adsorption process fits to the Freundlich model indicating that the adsorbent has a great affinity for sorbate (Hossain et al., 2012). Adsorption capacities (q_{max}) recorded by raw adsorbents were lower than those recorded by the quaternised adsorbents. This clearly shows that quaternisation improved the sorption capacities of these adsorbents. These results compare with those reported in study of quaternised maize tassels to remove chlorophenols (Mwangi et al., 2014), sewage sludge based activated carbons to remove PNP (Mohamed et al., 2011). The R^2 of 0.8931 obtained in RAM indicate applicability of Freundlich model for adsorption of PNP using this adsorbent. Freundlich model prescribes a multilayer adsorption which is a descriptive of both chemisorptions and physical sorption of PNP as a result of weak Vander Waal forces (Deng et al., 2003; Hossain et al., 2012; Mwangi and Ngila, 2012). Adsorption capacity and intensity are represented by constants K_f and n

respectively (Voudrias et al., 2002). From Table 1 the value of $\frac{1}{n}$ observed indicates cooperative adsorption of PNP by both RAM and QAM (Dada et al., 2012). The values for K_f for quaternised adsorbents are higher than those of the raw adsorbents as shown in table 1, thus indicating the efficiency of the quaternisation process. This could be due to improved surface texture and micro pore structure as well as increased adsorption sites hence higher adsorption capacity for QAM than RAM. The constants for the adsorption isotherms used in this study are presented in Table 1.

Table 1. Langmuir and Freundlich constants for PNP adsorption using raw and quaternised adsorbents

Ads	Langmuir isotherm			Freundlich isotherm			
	q_{max} (mg/g)	b (L/ mg)	R^2	K_f (mg/g)	n	R^2	Best model
RAM	8.70	0.2081	0.6076	2.85	0.02985	0.8931	Freundlich
QAM	106.38	0.11648	0.966	15.02	0.7170	0.0052	Langmuir

Table 2. Adsorption capacity of different adsorbent materials for the adsorption of PNP

Adsorbent material	q_{max} (mg/g)	Reference
Activated jute stick char	39.38	Ahmanizzaman and Gayatri (2010)
Salicylaldehyde modified chitosan	8.5	Abdel-Ghani et al. (2015)
Olive cake based activated carbon	1.550	Abdel-Ghani et al. (2016)
Activated carbon impregnated with Ni	12.48	(Matus et al. (2016).
<i>Acacia glauca</i> activated carbon	204.79	Prashant et al. (2016)
Pilli nut based activated carbon	190.39	Nwosu et al. (2017)
Biochar samples pyrolysed at 300 °C	5.711	Lanqi et al. (2020)
Biochar samples pyrolysed at 700 °C	117.165	Lanqi et al. (2020)
Cauliflower based activated carbon at 250 °C	13.28	Nidhi et al. (2020)
Sea mango activated carbon	158.73	Nurul et al. (2020)
RAM	8.70	Present study
QAM	106.38	Present study

The adsorption capacity obtained for QAM in this study was higher than the ones obtained with activated carbon synthesized from activated jute stick char (Ahmanizzaman and Gayatri, 2010), cauliflower waste (Nidhi et al., 2020), pine saw biochar olive cake (Abdel-Ghani et al., 2016) as well as activated carbon impregnated with Ni (Matus et al., 2016). This could be attributed to the efficiency of the modification process that anchors a positively nitrogen atom in the cellulose structure that bonds well with the negatively charged PNP ions. However, the value obtained for QAM was lower than the one obtained with activated carbon synthesized from acacia glauca sawdust (Prashant et al., 2016), pilli nut shell (Nwosu et al., 2017), sea mango (Nurul et al., 2020), pine saw dust biochar (Lanqi et al., 2020). The comparison of adsorption capacities of RAM and QAM with previously reported adsorbent materials is presented in Table 2.

CONCLUSION

In this study, adsorption efficiency of raw and quaternised *Fromomum melegueta* peels towards removal of PNP from water was evaluated. Removal efficiency of PNP is high at the first 30 mins of contact and at sorbent dosage of 0.01 g and 0.03 g for RAM and QAM respectively. Quantity of PNP removed increases as the initial concentration rises however, adsorption decreases after a concentration exceeding 30 mg/L. The ideal pH and temperature for PNP removal is at pH 3 and 25 °C respectively. Adsorption of PNP onto QAM and RAM follows Langmuir isotherm model and Freundlich isotherm model respectively. Raw and quaternised adsorbents showed different levels of efficiency in removing the PNP; quaternisation was shown to greatly improve the adsorption of PNP. A follow-up study is recommended on the adsorption kinetic studies as well as adsorption efficiency of the *Fromomum melegueta* peels for other phenolic compounds from environmental water samples.

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