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DISPOSABLE RESIDUE OF TRADITIONALLY FERMENTED ETHIOPIAN LOCAL BEER (*TELLA*) FOR QUANTITATIVE UPTAKE OF PESTICIDE POLLUTANTS FROM CONTAMINATED WATERS

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ABSTRACT: This major aim of this study was centered at developing a novel analytical method that enable quantitative uptake of multiclass pesticide pollutants from contaminated aqueous solution using a biosorbent obtained as a solid residue from fermented traditional alcoholic beverage; *Tella.* The solid residue considered in the study, also called Local Beer Residue (LBR) was first washed thoroughly under running water and then reagent water, and also treated with dilute hydrochloric acid solution. Presence and types of the functional groups on the LBR surface, that are facilitating analytes sorption, were analyzed using the FT-IR spectrometer, after processing to make a pellet with KBr. The effects of various experimental parameters on the biosorbent performances were studied and then optimized for maximum removal of the s-triazine family pesticides, such as atrazine, ametryn, secbumeton, propazine and prometryn. The established optimum conditions includes pH of 5.0, adsorption dose of 0.7 g, agitation speed of 250 rpm, contact time of 75 min and analytes concentration ranging within 0.25 to 1 mg/L. Furthermore, adsorptions of most analytes, considered in the study, were found to fit Langmuir adsorption model while two of them, *viz.*, prometryn and terbutryn following the Freundlich model. The experimental adsorption results were found fit the pseudo-second order kinetic model for all the studied analytes, certifying chemisorption to be the rate-determining step. It has also been understood that the acid treated residue of LBR to exhibit efficient adsorption capacity for quantitative removal of the target analytes considered. The novel LBR biosorbent developed in this study has further displayed remarkable performances its capacity for efficient removal of pesticide pollutants from contaminated water samples and thus can be used as effective, cheap, low-cost and locally available adsobent.

Keywords/phrases: FT-IR, local Beer Residues, pesticides, removal efficiency, water contamination

INTRODUCTION

Use of pesticides has been known and recognized as one of the cost effective methods of controlling pests and playing vital roles towards improving productivities and ensuring food security in modern agriculture. However, their high application rates, frequent and indiscriminate uses are noticed and reported to threaten human and animal health, and lives of the ecosystem (Buori *et al.,* 2012). This may mainly be due to the occurrence of maximum proportions of pesticides seasonally applied to the various environmental compartments including the plants, food and soil, and eventually moving into the atmosphere and water bodies (Tesfa Bedassa *et al.,* 2015). In most cases, the residual levels of both the parent pesticides and their degradation products are beyond the level that the environment can assimilate (Larsson *et al.,* 2011) and thus exceeding the maximum residue limits (MRLs) issued by various legislative authorities (Gonzalez-Curbelo *et al.,* 2012). To this end, a number of conventional and miniaturized analytical sample preparation techniques have been developed for selective and quantitative extraction of these residues from different water bodies in order to understand their levels of accumulation in various contaminated matrices (Tankiewicz *et al.,* 2011).

Apart from selective extraction of the pesticide residues, considerable efforts have also been made aiming at developing reliable analytical methods for carrying out efficient uptake of these compounds from various matrices of different origins; particularly in drinking, natural as well as underground water resources

(Ahmed *et al.,* 2010; Bhatnager and Minocha, 2006). In this regard, varied adsorption techniques based on membrane adsorption (Kozlowski and Walkowisk, 2002), activated carbon (Diaz-Flores *et al.,* 2006), chemical precipitation (Esmaeili *et al.,* 2005), carbon nano-tube (Tang *et al.,* 2012), iron nano-particles (Varanasi *et al.*, 2007), zeolite-supported TiO_2 (Shankar *et al.,* 2006), modified polymeric resins (Doulia *et al.,* 1997), have been developed and successfully utilized for removal of pesticides as well as selected heavy metals from different waters. However, most of these techniques have their inherent advantages and limitations. For example, techniques such as chemical precipitation and those requiring activated carbon usually produce large quantities of sludge and thus ineffective when concentration of the molecules to be removed, in the aqueous solutions, is lower than 50 mg/L (Bezuayehu Tadesse *et. al.,* 2015). On the other hand, techniques employing membranes and carbon adsorption are rather expensive while techniques such as biotransformation (Shaw and Burns, 1998) and catalytic degradation (Wang *et al.,* 1999) leave significant concentrations of the degradation products. Thus, use of biosorbents as promising alternative seems to owe several advantages and also circumvent the drawbacks associated to most adsorption techniques (Bhatnagar and Minocha, 2006). Biosorption is thus the process based on the use of biomasses that are safer, locally available, cost effective and/or possibly disposable, generating no by-product etc, and recently gained great attentions for efficient removal of chemical pollutants from various wastewaters and industrial effluents (Ahmed *et al.,* 2010; Bhatnager and Minocha, 2006).

Biosorption is a relatively recent technology in its use as adsorbent for removal of trace level organic and inorganic pollutants from contaminated streams utilizing inactive and dead biomasses (Zhang *et al.,* 2013). It can be considered as low-cost alternative than the conventional techniques. Improved efficiencies may mainly be due to their large surface area, high sorption capacity and surface reactivity. Some of the common biosorbents include materials that are locally available in large quantities such as microorganisms, natural materials, living or dead biomass, agricultural wastes or industrial by-products/wastes, used in pollutants uptake with quite little processing, fast adsorption kinetics, easily generable and good mechanical strength (Ahluwalia and Goyal, 2007). Their removal efficiencies are based on physical-chemical interaction between the substances in the matrices and one or more of the most commonly found functional groups present on the surface of the biomasses such as carboxylic, phosphate, sulfate, amino, amide and hydroxyl groups (Ahemed and Malik, 2012).

In this work, efforts were devoted to introduce a novel alternative sorbent material and investigate its potential as biosorbent, the residue obtained as a by-product after production of the traditionally fermented alcoholic beverage, *Tella* or Ethiopian Local Beer, has been considered. *Tella* is often a home-brewed liquor and is also one of the oldest traditional alcoholic beverage, most commonly consumed in almost all regional states of Ethiopia, during the holidays, annual celebrations, special festivity and church ceremonies, etc. Furthermore, the beverage is commonly consumed on the weekly market days of small or larger towns, by all groups of the community in several *Tella* vending houses. A report by Samuel Sahle and Berhanu Abegaz Gashie (1991) described that over two million hectoliters of *Tella* is produced annually in the households and *Tella* vending houses in Addis Ababa alone.

Tella, is prepared from various vernacular grains and is a malt beverage based on the substrates such as barley, wheat, maize, millet, sorghum, *Teff* or other cereals. Other ingredients used in the liquor preparation process include flours of the cereals for mixing with water; *Gesho* plant (*Rhamnus prinoides*), to impart the typical bitter taste to the drink; and wheat or barley for preparation of malt used for fermentation of the cereals. Common procedures for preparation of the drink and the relevant fermentation steps are described in detail by other workers (Samuel Sahle and Berhanu Abegaz Gashie, 1991; Belachew Desta, 1977; Mogessie Ashenafi, 2006). In this study, sedimented residue of the solid waste remained after complete draining and transfer of the liquor, also called Local Beer Residue (LBR), to another container was used for quantitative removal of pesticide residues from polluted water samples. Prior to the use of LBR , all the necessary chemical treatments were carried out. Furthermore, experimental parameters influencing performances of the LBR biosorbent efficiencies were also optimized. Adsorption isotherms as well as kinetics of the adsorption processes were also evaluated. Based on the observed results, application potentials of the LBR for use as promising and reliable alternative adsorbent have experimentally been confirmed.

MATERIALS AND METHODS

Chemicals and reagents

All the standards of *s*-trizine pesticides, considered in this study; *viz.*, atrazine, ametryn, secbumeton, propazine and prometryn were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). Acetonitrile was purchased from Carlo Erba (Rodano, Italy) and methanol from Sigma Aldrich (Seelze, Germany). Sodium hydroxide pellet was from BDH Laboratory Supplies (Poole, England) and hydrochloric acid from Sigma-Aldrich Chemie GmbH (Steinheim, Germany), were used to adjust the sample pH. Ultrapure water was obtained by purifying with double distiller, A8000 Aquatron water Still (Bibby Scientific, Staffordshire, UK) and deionizer (EASYPURE LF, Dubuque), and filtered under vacuum through cellulose acetate filter papers (0.45 µm, Micro Science). Stock standard solution of 100 mg/L of the target analytes was prepared in methanol. Intermediate standard solutions of 10 mg/L were obtained by diluting the standard stock solution. The working solutions of lower concentrations were prepared from the intermediate standard solution. All solutions were stored, in the refrigerator at 4^{o}C , when not in use.

Apparatus and instruments

Chromatographic analyses were performed using Agilent Technologies 1200 series HPLC, equipped with quaternary pump, Agilent 1200 series Vacuum Degasser, Agilent 1200 series Autosampler and Agilent 1200 series diode array detector (DAD); all purchased from Agilent Technlogies (Agilent Technlogies, Germany). Chromatographic separation of the target pesticides was performed on a ZORBAX Eclipse XDB-C_{18} analytical column (150 x 3 mm i.d., 3.5 µm particle size) (Agilent technologies, USA). Data acquisition and processing were accomplished with LC Chemstation software (Agilent Technologies). Sample solution pH was adjusted using Adwa pH meter, model 1020 (Romania) and orbital shaker (Model CHINCAN, WSZ–100, China) was also used for homogenizing the LBR throughout the sample solution during sample preparation. Identification of the various functional groups of the LBR , before and after loading with the analyte pesticides, was accomplished by the spectrum 65 FT-IR spectrometer (Perkin Elmer, USA). Both the fresh and pesticides loaded adsorbents were mixed with KBr (spectroscopic grade) and prepared as pellets for FT-IR analysis.

HPLC analysis

Chromatographic separations were carried out using ternary mobile phase; ultrapure water (45%), acetonitrile (20%) and methanol (35%) in isocratic elution mode at the flow rate of 0.5 mL/min. The column temperature was kept at 35^{o}C and the detection wavelength at 230 nm with band width of 4 in reference to wavelength 360 nm having bandwidth 100. Analyte analysis was achieved by injecting 10 µL of the sample as well as the extract solution. Separation of the target analytes was then achieved in 10 min run time followed by 1 min post time. Under these chromatographic conditions, a good baseline separation was obtained for all the target compounds. Quantitative determination of the instrumental responses was based on the peak areas.

Preparation of Ethiopian Local Beer, Tella

Traditional preparation of fermented alcoholic beverage vary from one region to the other and even within a given locality, as there are no established local or national standards of brewing the local beverages. However, the general procedure of mixing the ingredients, time required for fermentation as well as the sequences of processing and consumption are mainly similar. The various literatures (Samuel Sahle and Berhanu Abegaz Gashie, 1991; Belachew Desta, 1977) and a general review published on Ethiopian indigenous fermented foods and beverages (Mogessie Ashenafi, 2006) reported detailed descriptions of the preparation steps, microbiological studies and alcoholic contents of the home made food and drinks in Ethiopia. For the purpose of the current study, brewing of the Ethiopian Local Beer or *Tella* was processed and prepared at home, using the expertise of experienced ladies in the Addis Ababa city; the center and capital of the country, Ethiopia. The volunteer brewers were also asked to stick to the procedure most commonly followed and accepted by most local brewers.

The fermented drink or *Tella,* in most cases, becomes ready for consumption nearly in two weeks time (observed variations may be caused by geographical locations and weather conditions of the regions). When the drink is ready for consumption, it is the upper suspension or liquor which is separated by decantation and then be transferred to a clean clay pot for subsequently serving to the consumers, either at home or vending houses. After completely draining the liquor, the sedimented solid residue will be left in the container, i.e., traditionally clay pot, which is to be disposed commonly to the abandoned sites; far from the residence houses. It is this residue (named Local Beer Residues or "LBR ") that was considered and used as adsobent (or biosorbent) in this study after undergoing through different treatments (see next subsection). For use in further analyses, the residue was collected in the polypropylene bowls, brought to the laboratory and kept in the refrigerator at 4°C, for maximum of a day or two, before use.

Treatment and preparation of the Local Beer Residues (LBR)

In the laboratory, the LBR was first thoroughly washed under running tap water in order to remove any adsorbed soluble impurities such as trace coloring agents, soluble sugars, organic and inorganic compounds to the residue. Washing was continued until the color of water used for washing the LBR appeared clear and repeatedly rinsed with reagent water and finally with methanol (Memon *et al.,* 2007). The resulting residue was then dried under the shade, for three consecutive days, to protect from direct sun light. It was further dried in oven for maximum of 24 h at 80 °C, checking for the weight at interval of 2 h, until remained constant.

The fermented beverage prepared following the procedure given in the above subsection and the LBR biosorbent prepared according to the literature information (Samuel Sahle and Berhanu Abegaz Gashie, 1991; Belachew Desta, 1977; Mogessie Ashenafi, 2006) are given in the Figure 1.

Chemical modification of the biosorbent (LBR)

In order to investigate the effect of chemical treatment, on adsorption performance of the LBR , the method previously described in the literature (Memon *et al.,* 2008; Yadamari *et al.,* 2011) was followed. Briefly, 0.7 g portion of the dried LBR was first transferred to each of the three 200-mL volumetric flasks; the contents in the first flask was left untreated while those in the second and third flasks were treated with 50 mL solutions of 0.1 mol/L HCL and 0.1 mol/L HNO_3, respectively. The contents of the latter two flasks were heated for 4 h at 50°C and left to stand overnight. The resulting mixtures were then filtered, using Whatmann Filter Paper No.41; followed by washing and rinsing the LBR repeatedly with reagent water until pH of the washing solution remained constant at 7 ± 0.2. Afterwards, both the untreated and treated LBR were dried to constant weights and ground to fine powders using electrical grinder, which were subsequently sieved through 250 μm mesh. The ground and sieved particles were further dried in oven at 80°C for 180 min. Finally, the processed residues were stored in three different screw-capped glass bottles and kept in a desiccators until used as adsorbent materials.

Batch adsorption experiments

Batch experiments were carried out using a series of 100 mL conical flask to investigate the effects of pH, adsorbent dosage, contact time and initial pesticide concentrations on adsorption of the target pesticides from aqueous solutions. A weighed amount (0.7 g) of acid treated LBR or *Tella* residue was added to the conical flask with 25 mL of the mixture of pesticide solution of known initial concentration (1 mg/L) adjusted to pH 5. The content was then agitated at a constant speed of 250 rpm for 75 min on an orbital shaker and filtered.

The residual pesticide concentration in the solution was determined by the HPLC-DAD. The equilibrium concentrations of the pesticides, in the mixture, were determined based on the peak area measurement, using HPLC-DAD. Finally, the signals obtained as such were computed in terms of the pesticides concentration using standard calibration curve. In all cases, the adsorption capacity at equilibrium, q_e (mg/g), of each pesticides was calculated using the following relation; equation 1:

$$q_e = \left(C_o - C_e\right)\frac{V}{W} \qquad (1)$$

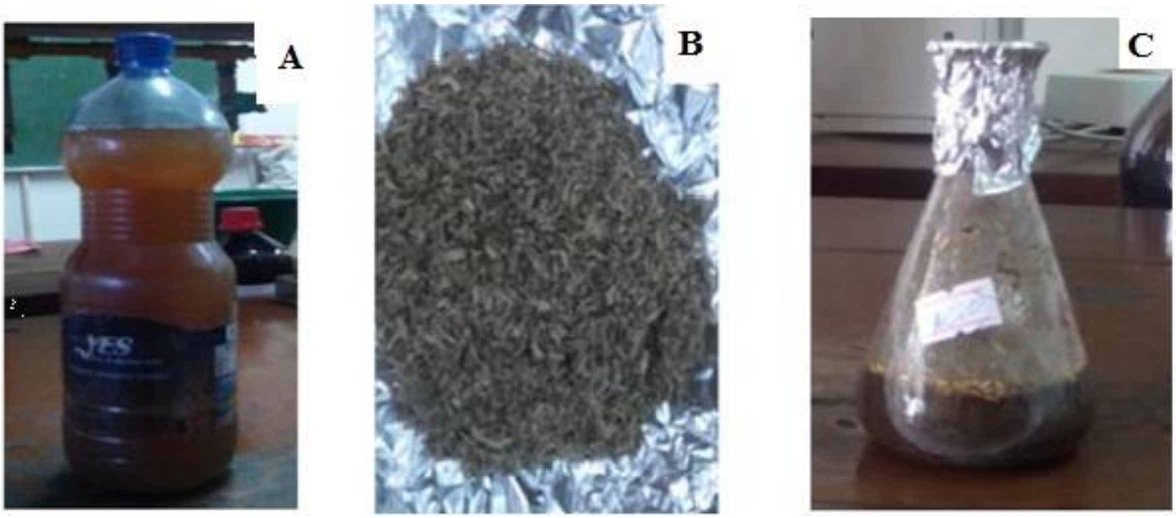

Figure 1. Representative photographs of (A) the fermented traditional alcoholic beverage, *Tella*, ready for consumption, (B) the solid residue leftover after separating from the liquor that is washed by tap and reagent waters, methanol and finally treated with dilute HCL, and (C) the acid treated solid residue used as biosorbent, i.e., LBR ; immersed in the aqueous solution contaminated with target pesticides.

where C_o and C_e (mg/L) are the initial and equilibrium concentrations of the pesticide compounds, respectively, 'V' is the volume (L) of the sample solution and 'W' is the weight of dry sorbent or LBR , in gram (g). Similarly, the percentage of pesticides adsorption on the LBR was determined utilizing the following equation (Bezuayehu Tadesse *et al.,* 2015):

$$\text{Adsorption} = \frac{C_o - C_e}{C_o} \text{ x } 100 \qquad (2)$$

RESULTS AND DISCUSSION

Characterization of the biosorbent

Since adsorption is a surface phenomenon, the rate and extent of adsorption specific to a given adsorbent are influenced by a number of physico-chemical characteristics of the adsorbent such as surface area, pore size, surface functional groups and composition. The pesticide-biosorbent interaction or binding process usually distinguished by the roles played by the functional groups present on the surfaces. The various groups, contributing significantly towards quantitative uptake, were identified by running the Fourier transform infrared (FT-IR) spectroscopy on the powdered LBR , prepared in KBr that was formed as a pellet (Singha *et al.,* 2011). Accordingly, in this study, the FT-IR spectra of the untreated LBR (A), LBR treated with 0.1 mol/L HCL (B) or 0.1 mol/L HNO_3 (C) and both loaded with pesticides were scanned within the frequency range of 4000–400 cm^{-1}. Large number of adsorption peaks has been observed on the spectra, indicating the complex nature of the studied LBR , Figure 2. As can also be seen from the vibration bands of the LBR , absorption peaks around 3400 cm^{-1} may be due to the presence of hydroxyl, O-H, group. Absorption peaks at about 2920 and 2780 cm^{-1} can be assigned to the stretching vibrations of the alkyl (C-H) and alkenyl (=C-H) functionalities, respectively. Similarly, peaks around 1740, 1620, 1340 and 1050 cm^{-1} have been observed may be due to the presence of C=O, C=C, O-H bending and C-O bond stretch, respectively (Bezuayehu Tadesse *et al.,* 2015). As shown in Figure 2, the major absorption peaks have undergone a change in their absorption bands, intensity and frequency, after loading with pesticides, confirming participation of these functional groups in the adsorption of pesticides on the LBR used as biosorbent in this study (Table 1).

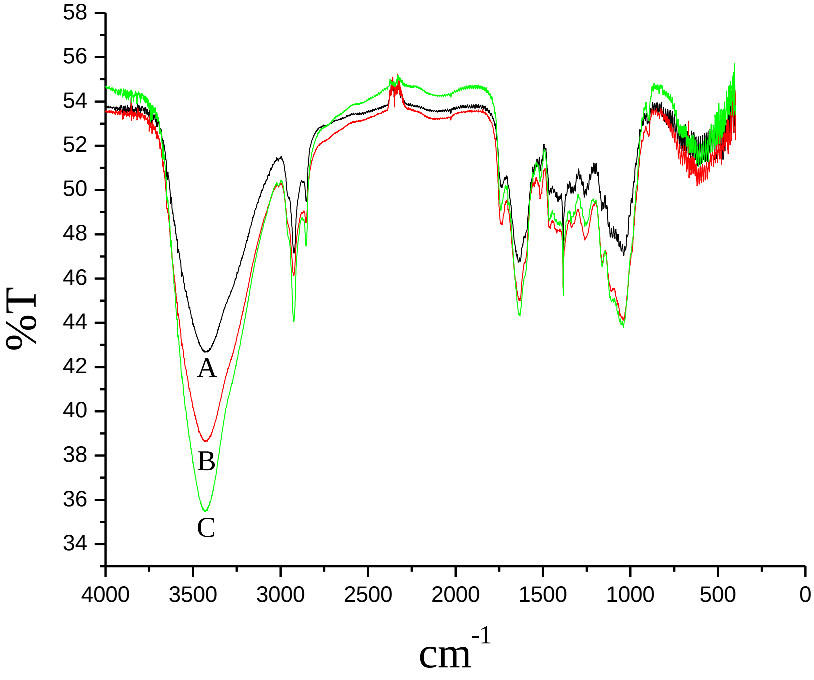

Figure 2. **FT-IR spectra of the LBR in KBr disc; before treating with acid (A), after treating with acid (B) and pesticide loaded after treatment (C).**

Table 1. The FT-IR spectral characteristics of the LBR before and after adsorption.

Before loading		After loading		Change	Functional group
cm^{-1}	%T	cm^{-1}	%T	in %T	Assignment
3408	38.8	3430	35.5	+3.3	hydrogen bonded O–H stretching
2923	46.1	2924	44.0	+2.1	alkyl C-H stretch
2781	52.8	2782	52.6	+0.2	alkenyl C–H stretch
1738	50.1	1740	49.1	+1.0	C=O stretching
1618	46.0	1636	44.4	+1.6	unsaturated C=C groups
1340	49.8	1338	48.5	+1.3	O-H bending
1053	44.3	1063	44.0	+0.3	C–O Stretching

Effect of the LBR surface modification

Acid treatment of the LBR biosorbent, using 0.1 mol/L of both HCL and HNO_3, significantly improved the degree to which the pesticides were removed from the aqueous solution compared to the untreated one (Memon *et al.*, 2007). Chemical treatment of both dilute acids exhibited similar increases in percent sorption of the analytes. However, HCL was selected to be used as surface modifier of the LBR adsorbent for all the subsequent experiments, mainly because of its availability in the laboratory, Figure 3. The improved removal efficiency of the target pesticides, after surface modification, can be attributed to the fact that the acid treatment may have dissolved the particulate matters, minerals and dirt from the biosorbent surface and thus increases the pore volume and surface areas of the adsorbent (Akhtar *et al.*, 2007).

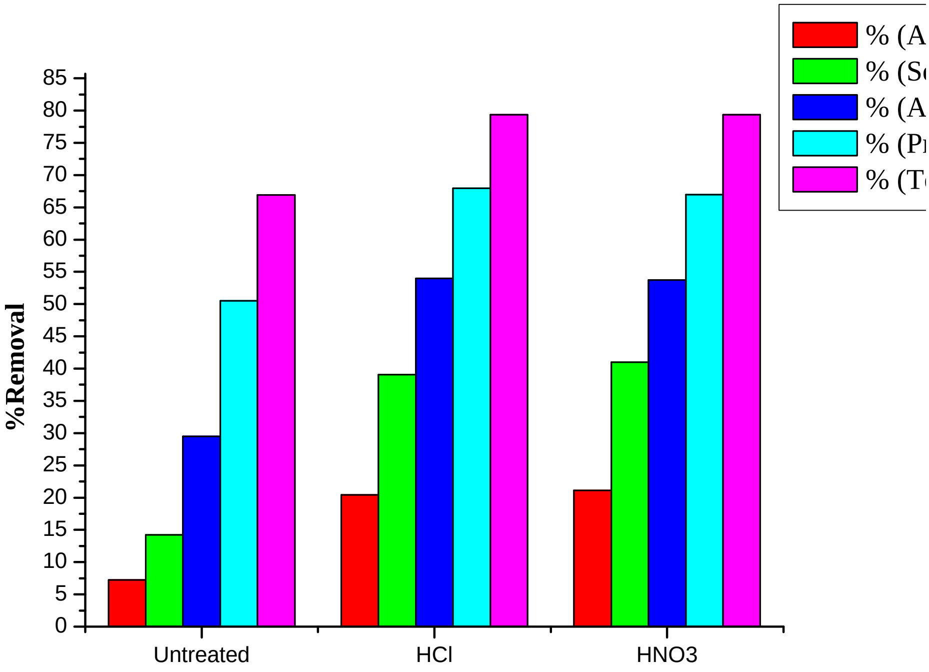

Figure 3. Effect of acid treatment of the LBR on the uptake of the pesticide analytes. Experimental conditions: sample size, 25 mL; spiked concentration, 1 mg/L; shaking speed, 100 rpm; contact time, 60 min; and adsorbent dosage, 0.3 g.

Effect of pH

The change in solution pH considerably changes the properties of pesticide molecules and as a result their adsorption becomes pH dependent. The surface functional groups of the adsorbent make adsorption complicated because of the charge characteristics of the adsorbent surface (Memon *et al.*, 2007). This effect may be more pronounced when a number of pesticides are to be removed from real polluted water samples. It is evident from this study that adsorption capacities of the pesticides from water samples, onto LBR , were strongly affected by the pH, Figure 4. It was also observed that removal efficiencies were increased with the increase in pH from 4 to 5 and then showed decreasing tendencies beyond pH 5. This may be due to deprotonation of the surface functional groups of the adsorbent which could result in more negatively charged carbon surface at higher pH than at the lower pH values (Negussie Megersa, 2015). The negative charge developed at the surface, as a result of deprotonation, may caused strong electrostatic repulsion for the pesticides in solution, thereby retarding diffusion and thus adsorption (Gupta *et al.*, 2011). Based on the experimental results, pH 5 was selected as optimum for all the subsequent experiments.

Effect of the adsorbent dose

The effect of adsorbent dose on the removal efficiency of the pesticides under investigation was studied by varying the mass of the LBR from 0.3 to 0.8 g. As it can also be seen from Figure 5, the pesticides adsorption exhibited increasing tendencies when the mass of LBR was varied in the range from 0.3 to 0.7 g, and displayed the highest adsorption capacity with 0.7 g. Beyond this quantity, adsorption of pesticides remained constant indicating that 0.7 g LBR adsorbent to be the optimal dose for removal of maximum concentration of the target pesticides. This thus suggests that the optimal dose experimentally found may be the limiting factor of adsorption sites available for adsorption at higher concentration of adsorbate molecules (Memon *et al.*, 2008).

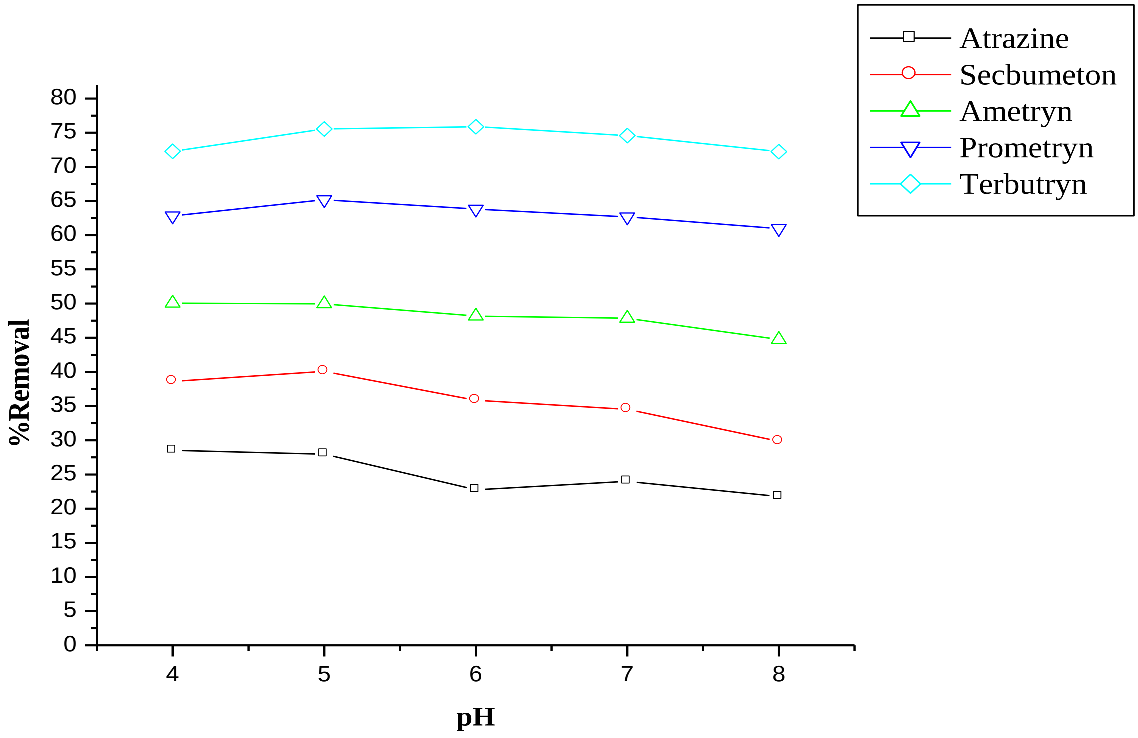

Figure 4. Effect of pH on the uptake of the pesticide analytes. Experimental conditions: sample size, 25 mL; spiked concentration, 1 mg/L; shaking speed, 100 rpm; contact time, 60 min; adsorbent dosage, 0.3 g.

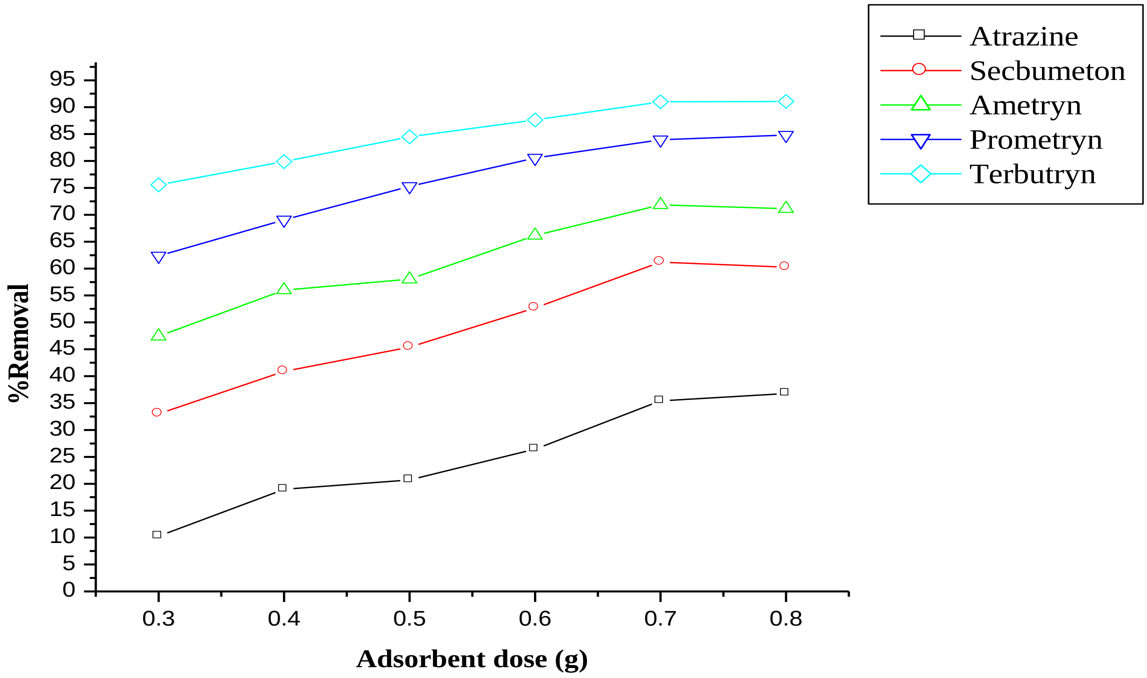

Figure 5. Effect of adsorbent dose on uptake of the pesticide analytes. Experimental conditions: sample size, 25 mL; spiked concentration, 1 mg/L; shaking speed, 100 rpm; contact time, 60 min; pH, 5.

Effect of the agitation speed

The increase in speed of agitation decreases the time required for the adsorbate to equilibrate, by decreasing the boundary layer resistance to mass transfer and hence increases the diffusion rate of the adsorbate from the bulk into the adsorbent particles (Bezuayehu Tadesse *et al.*, 2015). In this study, effect of the shaking speed on analyte adsorption was studied over the range of 100 to 300 rpm for 60 min; in a constant volume, 25 mL, of the aqueous sample containing 1 mg/L of each analyte compound. It has been observed that the percent adsorption increased with increase in the shaking speed and maximum adsorption was attained at 250 rpm for all analytes studied. At low and high speeds, the pesticides removal were found to be lower than the optimum. At lower speed than the optimum, the particles of LBR adsorbents might not sufficiently spread in the aqueous samples to ensure efficient contacts of the active binding sites for adsorption of the pesticides. Thus, lower shakings do not cause complete agitation of the adsorbents, and as a result the LBR particles may be accumulated at the bottom of water bed; the active binding sites may then be unavailable for adsorption. On the other hand, higher shaking speeds than the optimum may spread the LBR particles vigorously throughout the aqueous sample and therefore do not allow sufficient time for effective binding between the analytes and the adsorbent particles (Hossain *et al.*, 2012). Thus, 250 rpm was selected as optimum and employed for further experiments.

Effect of equilibration time

Effect of shaking time on percent sorption of the target analytes onto the LBR was studied over an agitation time of 45 to120 min. The experimental results revealed that removal efficiency increases with increase in shaking time.

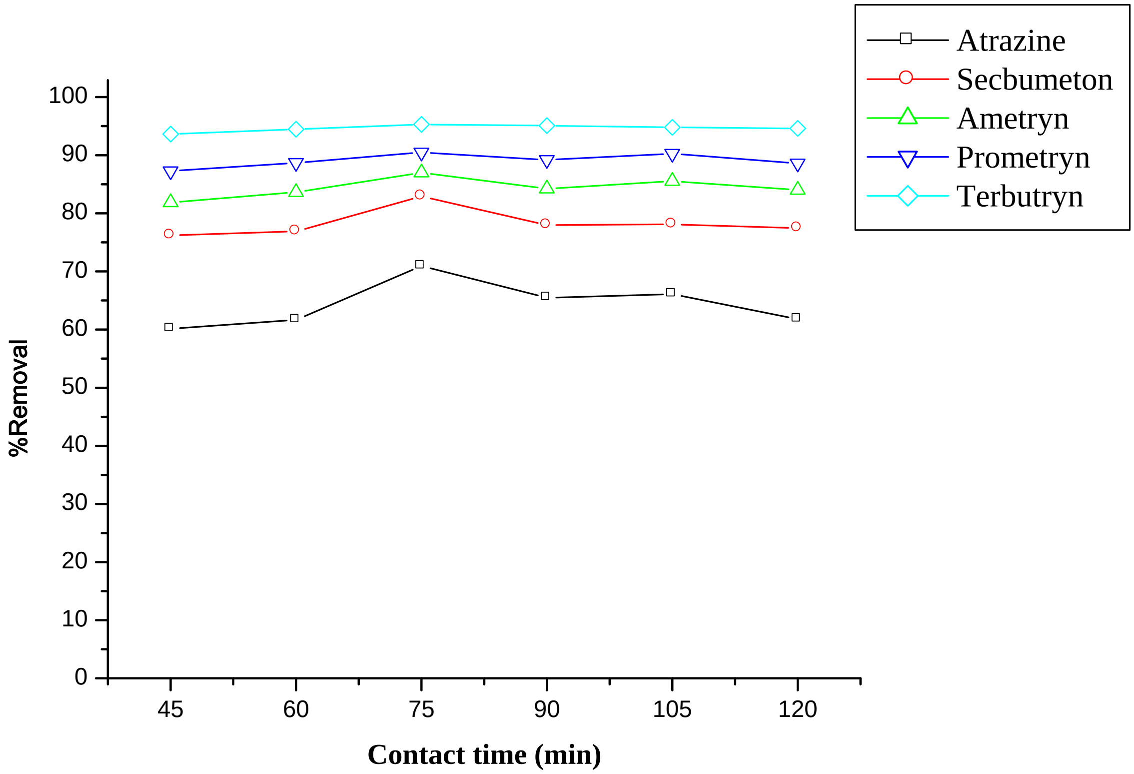

Figure 6. Effect of the contact time on the uptake of pesticide analytes. Experimental conditions: sample size, 25 mL; spiked concentration, 1 mg/L; agitation speed, 250 rpm; pH, 5; adsorbent dose, 0.7 g.

As shown in Figure 6, the equilibrium was established within 75 min for all the pesticide compounds considered in this study. However, it remained nearly constant after equilibrium time which could be attributed to saturation of the adsorbent surfaces beyond equilibration time (Rahmanifar and Dehaghi, 2014). As a result, 75 min of agitation time was found to be optimum and employed in all the subsequent experiments.

Effect of initial concentration of pesticides

The effect of initial concentration of the target pesticides on removal efficiency of LBR adsorbent was studied in the concentration ranging from 0.25 to 8 mg/L. It was then observed that with increase in the sorbate concentrations, corresponding decrease in removal efficiency was resulted, Figure 7, which may be caused by the limiting number of adsorption sites available for the analytes uptake at higher concentrations. This observation could also be associated to the sorbent to sorbate ratios, i.e., at low sorbate to sorbent ratios, target analytes sorption involves the higher energy sites, while at higher ratios the higher energy sites are saturated and sorption begins on lower energy sites, resulting in a decrease in adsorption capacity (Memon *et al.*, 2007).

Adsorption isotherm models

Basic physico-chemical information useful for evaluation of the extent of adsorption process may be derived from the sorption equilibria (Bezuayehu Tadesse *et al.*, 2015). In this context, the relationship between the amount of adsorbate and concentration in the aqueous solution, at equilibrium, can usually be expressed in terms of the sorption isotherm models. The most commonly employed models include, Langmuir and Freundlich models, utilizing mathematical equations for evaluating the precision of experimental data. In the same manner, the analytical results of the current study were also evaluated using these isotherm models (Muller *et al.*, 2012).

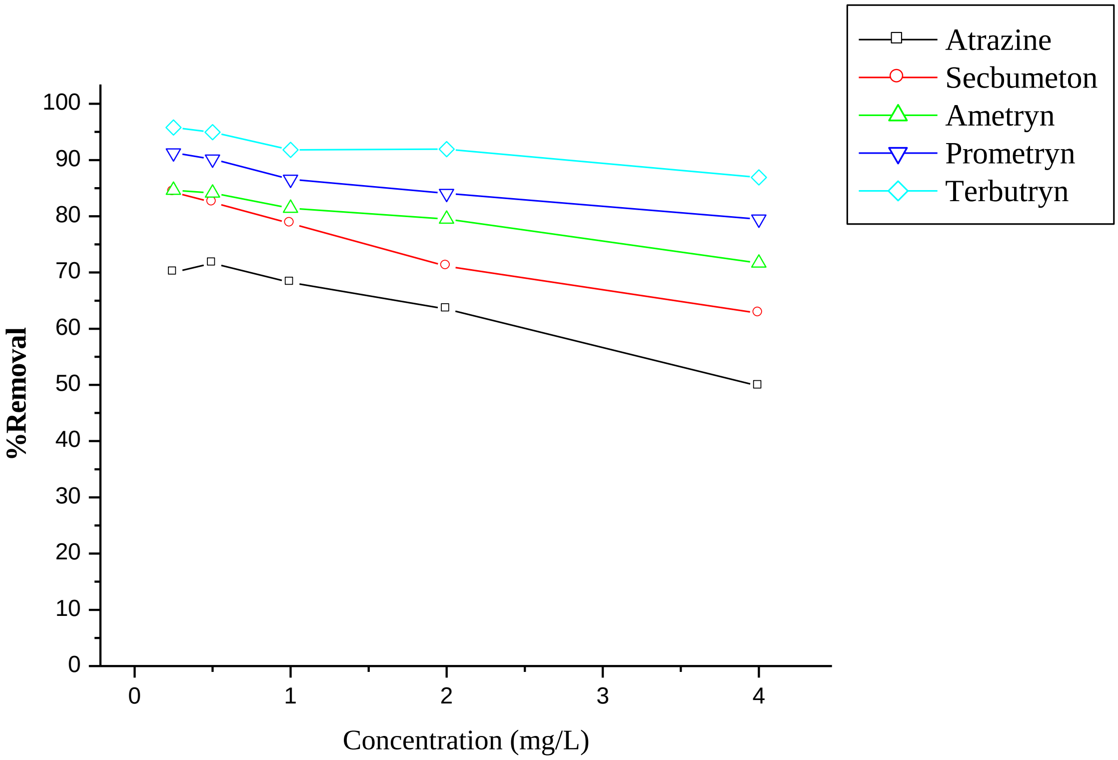

Figure 7. Effect of the analyte concentration on the uptake of pesticide analytes. Experimental conditions: sample size, 25 mL; spiked concentration, 1 mg/L; agitation speed, 250 rpm; pH, 5; adsorbent dose, 0.7g; contact time, 75 min.

Langmuir isotherm

The Langmuir model represents monolayer sorption on a set of distinct localized sorption sites with uniform energies and with no transmigration of sorbate in the plane of the surface. The sorption data obtained was applied by fitting the sorption results to the following linearized form of the Langmuir equation given below (Rozaini *et al.*, 2010):

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} x \frac{1}{C_e}$$

(3)

where q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium, q_e (mg/g) is maximum sorption capacity or uptake, C_e (mg/L) is the equilibrium adsorbate concentration in the solution and K_L (L/mg) is the Langmuir constant, which is related to the affinity of the binding sites for the adsorbate. The Langmuir parameters, q_{max} and K_L were calculated from the intercepts and slopes, respectively, of the linear plot of $1/q_e$ versus $1/C_e$ and the corresponding results are provided in Table 2.

Other characteristics, such as the shape of the Langmuir isotherm can be described in terms of the dimensionless quantity, defined as the separation factor, R_L. Its values for adsorption of the target pesticides onto the adsorbents were calculated using the following relation:

$$R_L = \frac{1}{1+K_F C_i} \qquad (4)$$

where K_F is obtained from the Langmuir plot and C_i (mg/L) is the initial concentration of the target analytes. In this study, calculated values of the separation factor for all the target analytes considered lied within the range of 0 and 1, which implies a favorable adsorption, Table 2 (Abdullah and Prasad, 2009).

Freundlich isotherm

The Freundlich sorption isotherm is an empirical expression describing the exponential distribution of active centers, characteristic of heterogeneous surfaces and infinite surface coverage. The linearized form of Freundlich isotherm is described using the following equation (Hasan *et al.*, 2008):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

where K_F is the Freundlich constant describing the adsorption capacity and representing the strength of the adsorptive bond; 'n' is a characteristic constant representing the heterogeneity factor for the bond distribution and adsorption intensity (Hasan *et al.*, 2008; Garcia-Rosales and Colin-Cruz, 2010); q_e and C_e stand for their usual significances defined earlier. The numerical values of K_F and 1/n would be computed from the straight line obtained by plotting log q_e versus log C_e; with the slope representing 1/n and intercept log K_F, and the results are given in Table 2. The value of 1/n < 1 indicates that adsorption capacity is slightly reduced at lower equilibrium concentration. However, close evaluation of the values of the regression coefficients, (R^2), the equilibrium data fit better to the Langmuir isotherm model for atrazine, secbumetone and ametryn indicating monolayer homogeneous surface conditions. On the other hand, prometryn and terbutryn fit Freundlich adsorption model indicating heterogeneous surface conditions.

Table 2. Experimental values determined for the Langmuir and Freundlich adsorption parameters.

Analyte	Langmuir parameters			Freundlich parameters		
	q_{max} (mg/g)	R_L (L/mg)	R^2	K_F ((mg/g)/(mg/L)$^{1/n}$)	1/n	R^2
Atrazine	5.291	0.417	0.996	1.40	0.736	0.985
Secbumeton	3.106	0.321	0.996	2.113	0.692	0.995
Ametryn	5.348	0.250	0.999	2.965	0.788	0.995
Prometryn	3.584	0.205	0.999	3.873	0.733	0.998
Terbutryn	3.257	0.136	0.993	6.339	0.721	0.992

Adsorption kinetics

Adsorption kinetic is a very useful characteristic for evaluating the adsorption efficiency and thus describing the rate of solute adsorption (Vinodhini and Das, 2010). Adsorption processes are generally governed by the sorption mechanism and the reaction rate, the latter determining the residence time required for completing the adsorption process which can be obtained from kinetic analysis. The mechanism of sorption and the rate-controlling step, caused by mass transfer and chemical reaction processes, are commonly evaluated using kinetic models for testing of the experimental data. To this end, in this study, the pseudo-first and pseudo-second order models were applied in order to investigate the mechanism of adsorption.

Pseudo first-order kinetics

Integrating the rate equation for the pseudo-first order kinetics and rearranging for the boundary conditions; 't' = 0 to 't' = t and q_t = 0 to q_t = q_t , a linear equation of the following form may be obtained (Malik, 2004):

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \qquad (6)$$

where q_t (mg/g) is the concentration of the target pesticides adsorbed at time 't' (min) and k_1 (min^{-1}) is the rate constant for the pseudo-first order equation. The linear equation obtained from the plot of log (q_e - q_t) versus 't' gives the slope and intercept that correspond to the values of q_e and k_1, respectively. The corresponding values of these variable are given in Table 3.

Pseudo-second order kinetics

For adsorption kinetics that follow the pseudo-second order mechanism, the basic rate equation (Bezuayehu Tadesse *et al.,* 2015; Malik, 2004) can be integrated for the boundary conditions; 't' = 0 to 't' = t and q_t = 0 to q_t = q_t , and rearranged to give a linear relationship of the form given below (Ho and McKay, 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \qquad (7)$$

where k_2 (g/(mg.min)) is the second-order rate constant and q_e is the equilibrium adsorption capacity for the pseudo-second order equation (Ho and McKay, 1998). The plot of t/ q_t versus 't', gives a straight line graph from which numerical values of q_e and k_2 would be determined from the slope and intercept, respectively (Kumar and Kirthika, 2009), and the corresponding values of the kinetic parameters as well as the regression coefficients (R^2) for the pesticides considered in this study are given in Table 3.

Table 3. Pseudo-first and second order parameters.

Analyte	Pseudo-first-order				Pseudo-second-order		
	q_e *(mg/g)	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/(mg min))	R^2
Atrazine	0.709	0.124	0.0046	0.274	0.643	2.248	0.990
Secbumeton	0.829	0.075	0.0023	0.617	0.784	1.476	0.999
Ametryn	0.870	0.069	0.0092	0.491	0.851	1.692	0.999
Prometryn	0.905	0.054	0.0161	0.272	0.903	0.966	0.999
Terbutryn	0.953	0.020	0.0138	0.301	0.987	0.239	0.998

q_e ***, experimental value***

It is evident from Table 3 that the correlation coefficient, R^2, values observed for the pseudo-second order adsorption model for the analytes of interest are relatively high (≥ 0.99) and the adsorption capacities calculated, using the model, are also close to those determined by the experiments. Therefore, the adsorption of the pesticide compounds considered on the LBR was found to favorably follow the pseudo-second order kinetic model which also relies on the assumption that chemisorption or chemical adsorption is the rate-determining step (Ibrahim *et al.*, 2006).

CONCLUSIONS

The novel biosorbent, obtained from the solid residue of fermented traditional alcoholic beverage; locally called *Tella*, was utilized for quantitative uptake of multiclass pesticides from contaminated aqueous solution. Before using the residue as a potential adsorbent, it was thoroughly washed under running tap and ultrapure waters, and then treated with dilute solution of hydrochloric acid. The surface properties of the biosorbent, named 'Local Beer Residue' or LBR , was investigated by first mixing with KBr, which was formed as a pellet. In doing so the various functional groups responsible for adsorption were identified by running the untreated, chemically treated LBR before and after loading with the target analytes, using FT-IR spectrometer. Furthermore, the effects of experimental parameters influencing the extent of adsorption on the LBR were investigated and the optimum conditions have been established.

The studied biosorbent has admirable adsorption capacities for the removal of multiresidue pesticides including atrazine, secbumeton, ametryn, prometryn and terbutryn. The results obtained revealed the LBR adsorbent to exhibit rapid adsorption rate and good adsorption capacity for the target pesticides. The adsorption of most analytes was found to fit the Langmuir isotherm suggesting monolayer coverage of the adsorbent surface. However, prometryn and terbutryn fit more to Freundlich adsorption model indicating monolayer sorption with a heterogeneous energetic distribution of the active sites. The kinetic study also revealed that adsorption process, of the present study, to follow pseudo-second order model indicating chemisorption as the rate-limiting step. Acid treated LBR residue is more effective, efficient, cheap adsorbent and can be used for reliable quantitative removal of the reported and other pesticides, possessing similar physico-chemical characteristics, from contaminated waters. In order to realize larger scale applications of the investigated biosrbent, experimental parameters relevant to the column adsorption technique should be considered and studied, along with its advantages and sustainability, for extending future uses of the LBR .

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