Pb(II) removal in water via adsorption onto deep eutectic solvent fabricated activated carbon

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Abstract
In our current work, we have established a novel approach in the synthesis of a new adsorbent by using choline chloride and urea (DES)/orthophosphoric acid (H3PO4) as our activating agent and palm kernel shell (PKS) as our precursor. The resulting activated carbon (DES/H3PO4-6002:3) was used to adsorb Pb(II) from aqueous solution. Characterization of DES-H3PO4-6002:3 by nitrogen adsorption/desorption isotherm measurements, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) demonstrated good micropores structure and high surface area that makes DES/H3PO4-6002:3 a suitable alternative for liquid phase adsorption. The fundamental batch experiment of DES/H3PO4-6002:3 was investigated by different parameters (such as concentration, pH, temperature and absorbent dose). The results obtained indicated that Langmuir model and pseudo-second-order equation best fit the data, indicating that the adsorption was controlled by chemical reaction and monolayer uptake. In addition, the fabrication of DES/H3PO4 AC exhibits good potential for Pb(II) ions uptake, including its high adsorption capacity (97.1 mg/g) and good recyclability. The future potential of this works lies in the identification of alternatives to environmental benign synthesis AC and reuse of Pb(II) ion–laden biosorbent after heavy metal uptake.

Keywords DES/H3PO4 · Pb(II) · Adsorption · Reusability · Palm kernel shell

Introduction
Presently, pollution of water ecosystem with heavy metal ions is a global problem considering the long-term risk both to the human well-being and to the environment. Due to industrialization, untreated or partially treated water is discharged into public land from sewage treatment plants containing toxic compounds, so water is polluted every day (Inamuddin and Ismail 2010). Lead, one of the major constituents in aqueous waste, is a priority pollutant (as considered by USEPA) (Pei et al. 2019) and has a legacy of being accumulative poison of ecological succession and bioconcentration (Pei et al. 2019). The allowable concentration of Lead ions in wastewater (WHO approved) is approximately 0.01 mg/L (Kumar et al. 2019). Moreover, long exposure to lead especially at acute level could shut down the biochemical pathways causing damage to the central peripheral nervous (Alghamdi et al. 2019; Penugonda et al. 2006), kidney (Boskabady et al. 2018; Wani et al. 2015), reproductive system of persons (Fenga et al. 2017), often leading to death as sequelae of lead poisoning. The release of Pb into water ecosystem is often due to discharge related to certain
industrial units, including battery manufacturing (Alghamdi et al. 2019; Jan et al. 2015), mining (C. P. Wang et al. 2011a, b), smelting (Edokpayi et al. 2015), oil refining (Alghamdi et al. 2019) and so on located in close proximity to the water bodies. In addition to industries, another concern is corrosion of plumbing materials (water pipes) (Boskabady et al. 2018) and lead applications in agriculture (in fertilizers and pesticides) and in leaded gasoline (Jan et al. 2015). Application of conventional methods (electrochemical treatment, precipitation, reduction, membrane separation and so on) in the treatment of water with metal ions has some drawbacks (secondary pollution, high cost of operation and low efficiency), and adsorption onto suspended particle has shown to be cost-effective and efficient method (Fiyadh et al. 2019; He et al. 2019). Different adsorbents, including clay (Yin et al. 2018), carbon nanotubes (Dai et al. 2018), nano-TiO2/cellulose composites (Zhang et al. 2016) and activated carbon (Kyzas and Mitropoulos 2018), are well exploited in Pb ions removal in water. Activated carbon, among various adsorbent, is a well-developed porous material with an excellent performance, and immense process applications (Ahmed et al. 2019) are widely utilized alone or alongside other materials for the treatment of lead in water (Kumar et al. 2019). Activated carbons prepared from activating reagents including KOH, ZnCl2 and NaOH are usually not compatible with food industries and have high tendency for secondary pollution. To solve this problem of environmental and health concern, deep eutectic solvents (DESs)/H3PO4 activated carbon was fabricated. Deep eutectic solvents (DES) are solvents with almost no toxicity, high recyclability, low inflammability and volatility, and total biodegradables are promising sustainable alternatives to ionic liquids and conventional solvents (Di Gioia et al. 2018). In addition to the environmentally friendly properties of DES, they are also easy to prepare (Kumari et al. 2018). These fascinating physical properties and the freedom to design DES play a vital role in many field applications, including separation, preparation of inorganic and organic materials, extraction, biotransformation, nanomaterial, electrochemistry (Kumari et al. 2018) and interactions with other compounds by surface modification, thus providing a suitable podium for functionalization, synthesis and development of adsorbents with green chemistry framework. The potential applications of DES in water treatment can be seen in functionalization of carbon nanotubes, graphene and graphene oxide, and carbon monoliths (Carriazo et al. 2012; Huang et al. 2015; Lawal et al. 2019; Wang et al. 2017) and in the synthesis of composite materials (Chen et al. 2017; Patiño et al. 2012; Tang and Row 2019).

Palm kernel shell (PKS) is an unavoidable by-product of palm oil milling industry and is disposed of by burning or dumping into open environment, which wastes as valued resources and equally causes environmental pollution. Converting PKS to activated carbon is the right direction as it will not only solve the disposal problems associated with PKS, but also serve as renewable alternative precursor for the traditional fossil fuels for preparation of activated carbon. Taking into cognizance the need for a renewable and benign adsorbent for water treatment, we exploited the unique properties of chloride chloride (DES)/orthophosphoric acid (H3PO4) as new and clean approach for the preparation of activated carbon using PKS as a precursor. H3PO4 is well known for its eco-friendly and non-polluting nature (Sivachidambaram et al. 2017).

The study aims at converting PKS to activated carbon using DES/H3PO4. Additionally, promising characteristics of DES/H3PO4 activated carbon as a lead adsorbent was evaluated via sequences of parameters (i.e., initial pH, dosage, initial concentration and temperature) in relation to lead separation mechanism in water. The findings, which are the first study on the application of DES/H3PO4 in the synthesis of AC, will help to produce environmental benign AC with promising removal capacity for heavy metals in practical industrial application and promote the use of renewable alternative precursors.

Materials and methods

Materials

Lead(II) salt (Pb(NO3)2), hydrochloric acid (HCl), sodium hydroxide(NaOH), all of analytical grade were supplied by Fisher Scientific, Pittsburg, PA, USA. Chlorine chloride (ChCl), and urea ≥ 98% as revealed by the supplier (Sigma-Aldrich, St. Louis, Mo, USA), and orthophosphoric acid (concentrated H3PO4, Merck, Germany). Synthetic wastewater (containing Pb) was obtained by dissolving stoichiometric amount of the Pb salt in ultrapure H2O to obtain a stock solution (1000 mg/L), and successive dilutions were made for working solution in subsequent batch experiments.

Preparation of deep eutectic solvent

To synthesis the DES, we used the method reported by Yadav and Pandey (2014). In a typical experiment, urea and choline chloride were mixed in mole ratio 2:1. To afford clear and homogeneous solution, the mixture was further stirred under heat at 80 °C. The deep eutectic solvent was then used in the preparation of activated carbon. The synthesis of the DES may be represented schematically as shown in Fig. 1a.
Activated carbon preparation

To prepare the activated carbon, the experiments were conducted in three basic steps, i.e., pretreatment, impregnation and activation as depicted in Fig. 1b. The dirt particles associated with the surfaces of the PKS were removed by washing with distilled water. The washed PKS was tried under sun for about 3 days, and then, the particles size of the PKS was reduced by crushing. The activating agent (DES/H$_3$PO$_4$) was obtained by mixing choline chloride/urea (DES) and H$_3$PO$_4$ by mass (2:3 and 1:4) and for period of 3 h stirred at 25 °C. DES/H$_3$PO$_4$: PKS ratio stood fixed at 2:1. The impregnated samples were introduced into a tubular furnace and carbonized to a temperature of 500 and 600 °C differently, at a constant heating rate of approximately 10 °C/min under continuous nitrogen flow. The holding time of the various carbonization temperatures was 2 h. After the reaction time elapsed, the samples were removed from the furnace and allowed to cool under room temperature, then washed with hot distilled water severally to remove the residual acid and then dried in an oven at 100 °C to a constant weight. The resulting activated carbons were ground and collected in sample bottles for further characterization and adsorption test. A preliminary adsorption test showed that AC samples prepared at impregnation ratio of 2:3(DES:H$_3$PO$_4$) and temperature of 600 °C donated as DES/H$_3$PO$_4$-600 2:3, demonstrated better capacity for the adsorption of Pb in aqueous solution than that of DES/H$_3$PO$_4$-500 2:3, DES/H$_3$PO$_4$-500 1:4 and DES/H$_3$PO$_4$-600 1:4 (data not reported). As a result, DES/H$_3$PO$_4$-600 2:3 was further analyzed using XPS Kratos Axis UltraDLD with ejected photoelectron having a monochromated beam Al Kα X-ray energy source (1486.7 eV). The resulting spectra were referenced by the C1 (graphitic carbon) peak occurring at 284.6 eV (Palomo et al. 2019) using the software package (XPSPEAK41). TGA was conducted using thermogravimetric analyzer (STA600 Perkin-Elmer) over a temperature range of 0–900 °C under nitrogen flow at heating rate of 10 °C/min.

Batch adsorption experiments

To appraise the practical application of DES / H$_3$PO$_4$-600 2:3 in Pb adsorption batch experiments were tested. Achieving this goal, we conducted series of batch adsorption experiments by varying the process factors. For the dosage optimization test, we varied the adsorbent masses from 0.1 to 0.3 g. For effect of Pb initial concentration, individual metal solution of 75 to 125 mg/L of Pb was used at fixed adsorbent mass. 0.1 M either of HCl or NaOH was used to examine effect of solution pH by adjusting the metal solutions pH to the anticipated values by a pH meter, while effect of temperature was investigated between 30 and
50 °C. All experiments were done in duplicate at fixed agitation speed of 150 rpm and metal solution of 200 mL. The residue Pb in the filtrate from the suspension was analyzed using atomic adsorption spectrophotometer (thermo Scientific-s series). The amount removal (qt) and uptake rate (%) of the AC were computed according to equations in (2) and (3), respectively:

\[
Q_t = \frac{(C_o - C_e)}{V/M}
\]  

(2)

Removal (%) = \(\frac{(C_o - C_e)}{C_o} \times 100\)  

(3)

where \(C_o\) (mg/L), \(C_e\) (mg/L), \(V\) (L) and \(M\) (g) stand for initial concentration, equilibrium concentration, volume of sample and weight of EDS/H\(_3\)PO\(_4\)-600 2:3.

Results and discussion

Characterization

Figure 2a shows the nitrogen adsorption–desorption isotherm of DES/H\(_3\)PO\(_4\) 600:3. The isotherm belongs to type 1 according to IUPAC classification, a typical characteristic of a microporous adsorbent. This result is supported by the PSD illustrated in Fig. 2b. Accordingly, the PSD appeared between 6.0 Å and 16.0 Å with a value of 11.0 Å (average pore diameter) and a total pore volume of 0.6181 cm\(^3\)/g, an indication of a microporous adsorbent. The apparent surface area estimated by BET method was 1413 m\(^2\)/g. Similarly, Su and Wang (2007); Foo and Hameed (2012); Nowicki et al. (2016) reported specific surface areas of 1423 m\(^2\)/g.

![Figure 2](image-url)
1496 m²/g, 1436 m²/g, for ACs that were prepared from Wood sawdust, rayon-based knitted fabrics and coffee. There is also a literature report of lower surface areas adsorbents (Danish et al. 2011; Das et al. 2015; Kyzas and Mitropoulos 2018). Table 1 presents the porous parameters of DES/H₃PO₄ obtained from nitrogen adsorption and the carbon yield. The DES/H₃PO₄ reported a yield of 30.7%.

The FESEM micrographs of DES/H₃PO₄ are shown in Fig. 2c. Evidently, the image shows porous structure that is well developed with large number of cavities of distinct sizes. The various cavities are helpful as they provide the channels for the entrapment of Pb(II) particles. As shown in the figure below, some of the pores were clogged by the H₃PO₄ and could be as a result of unliberated volatiles during the carbonizations process (Usman et al. 2013).

To enable the application and product quality of the DES/H₃PO₄-600 2:3, the thermal stability was investigated by TGA. The TGA curve is presented in Fig. 3a. The AC has three thermal degradation steps within the investigated range, which can be described based on their chemical composition. The first step observed around 100 °C could be ascribed to physically bound water. This was followed by the major weight loss between 200 to 400 °C, while some of the hemicellulose and cellulose were decomposed (Yao et al. 2016). The final stage, which was slow, observed around 400–900 °C, is related to the degradation of lignin in palm kernel shell (Yao et al. 2016). There was about 30% mass loss of the lignin within the investigated temperature. This is against 50% mass loss of the lignin reported by Klapiszewski et al. (2017) using ionic liquids. This shows that the activating agents (DES/H₃PO₄) have a chemical transformation effect on the thermal stability of the biopolymer.

For qualitative characterization of surface groups, FTIR spectra were collected and result analysis is presented in Fig. 3b. The spectra of the DES/H₃PO₄-6002:3 contain peaks in the region of 1061, 1158, 1650, 1742, 2900 and 3248 cm⁻¹ that are related to C–O group, P=O (in phosphate and polyphosphate) and O–C stretching vibration (in P=OOH and P–O–C linkages), –NH stretching of secondary amine group, C=O, CH and OH stretch vibration (Al-malack and Basaleh, 2016; Danish et al. 2011; Fahmi et al. 2018). With adsorption of Pb onto DES/H₃PO₄-600 2:3, there was a relative change in intensity of the bands and disappearance of some bands compared to the pristine DES/H₃PO₄-600 2:3 (Fig. 3c). This an indication the distorted bands partici-pated to some extent in the removal of Pb(II)ions (Tang et al. 2017). The peak intensity of OH, NH, C=O and phosphate groups obviously increased after adsorption of Pb, which properly could be due to H⁺ from carboxyl, hydroxyl or phosphate groups of DES/H₃PO₄-600 2:3 surfaces exchanging with Pb(II) ions, while NH₃, –OH or C=O could provide the needed electrons for surface complexation with Pb(II) ions through formation of coordination bond with oxygen or nitrogen (Huang et al. 2014).

To further elucidate the reactions on the DES/H₃PO₄-600 2:3 surface, the sample was analyzed using XPS. The C1s spectrum of EDS/H₃PO₄ is fit with two peaks

| Table 1 | Apparent surface area and porosity structural parameters for the DES/H₃PO₄-600 2:3 |
|---------|-------------------------------------------------------------------------------------------------|
| Adsorbent | AC yield | Surface area m²/g | Micropore volume cm³/g | Total pore volume cm³/g | Average diameter Å |
| DES/H₃PO₄-600 2:3 | 30.1 | 1413 | 0.5980 | 0.6181 | 11.002 |

Fig. 3  a TGA/DTG analysis curves DES/H₃PO₄-600 2:3 based activated carbon; FTIR of AC-600 2:3,  b before adsorption,  c after adsorption
at 284.6 and 285.7 eV (Fig. 4a), allotted to adventitious carbon (C–C/C=C) (Liu et al. 2018a, b, c) and C–H species (Kapilov-Buchman et al. 2017), respectively. The band gotten by spectra deconvolution O1s is presented in Fig. 4d. The peak positioned at 532.0 eV is attributed to C–O and/or P–O bonds (Zhao et al. 2014), while 530.5 (C=O in quinones), 532.7 (chemisorbed H₂O) (Li et al. 2015), 533.2 eV (P–O–P bonds) (Li et al. 2015) and 534.3 (COH, –COOH, –N–O–N–) (Li et al. 2014). The fitting curve analysis for N1s band was resolved into four peaks. The binding energies at 398.4, 399.4, 400.1, 400.8 and 401.9 eV are attributed pyridinic nitrogen (Chen et al. 2018; Kapilov-Buchman et al. 2017), –N=C group (Yang et al. 2012), pyrrolic nitrogen (Chen et al. 2018), graphitic nitrogen (Kapilov-Buchman et al. 2017) and graphitic2 nitrogen (Kiuchi et al. 2016). Curve fitting analysis for P 2p shows main component with BE = 131.4–133.9 eV ascribed to phosphate species on the DES/H₃PO₄-600 2:3 surfaces related to P–atom bonded to O and C-atoms or phosphate likes structures, which agrees with the FTIR result. Besides, the P 2p spectrum was resolved into five components. The band energy at 133.50 represents P=O (L. Liu et al. 2018a, b, c), the two peaks at 131.4 and 132.8 eV binding energy are related to the P–C bonding (Hou et al. 2017; J. Wang et al. 2018), while peaks at 133.1 and 133.9 eV binding energy correspond P–O (Liu et al. 2018a, b, c; Wang et al. 2018).

The functional groups on DES/H₃PO₄-600–2:3 would give rise to the adsorption properties of the biosorbent. Oxygen-containing groups (–OH, –COOH, –ROH) and nitrogen functional groups (Mi et al. 2019) of adsorbents surfaces, apart from surface area and pore volume, contribute significantly to the adsorption process. Moreover, both pyridinic nitrogen and pyrrolic nitrogen (Mi et al. 2019) and phosphate groups (Liu et al. 2018a, b, c) on the adsorbents are reported to influence heavy metal ion removal. It is expected that the properties of DES/H₃PO₄-600 2:3, including porosity, functional groups would have had influential effect on the efficacy of DES/H₃PO₄-600 2:3 during the adsorption of Pb(II) ions from aqueous solution. Moreover, changes observed after adsorption of lead on the FTIR could be an indication of some of these functional groups participating in removal of Pb(II) ions.

**Fig. 4** XPS spectra of EDS/H₃PO₄-600 2:3. a wide scan, b C 1s spectra, c N 1s spectra, d O 1s spectra and e P 2p spectra
Adsorption characteristics of lead on DES/H₃PO₄-600 2:3 dosage

In order to ascertain removal capacity of DES/H₃PO₄-600 2:3 for a given lead initial concentration in aqueous solution, the effect of adsorbent dosage was examined. It can be seen that increase in adsorbent dosages concentration in the range 0.1 to 0.3 g leads to significant increase in active sites concentration, leading to a corresponding removal efficiency of Pb(II) from 36.0 to 50%. However, a decreasing trend in the adsorbed amount of Pb per unit mass of DES/H₃PO₄-600 2:3 from 38.1 to 16.6 mg/g was observed by the same dosage variation, which could be attributed to unsaturation sorption sites present on the adsorbent due to decrease in the quantity of Pb(II) to available sorption sites. The effect of varying DES/H₃PO₄-600 2:3 dosage on Pb(II) removal is shown in Fig. 5. Thus, considering efficiency and economy (Liu et al. 2018a, b, c), we considered 0.20 g/mL as optimum DES/H₃PO₄-600 2:3 load to assess the effect of other parameters in later experiments.

Effect of concentration and contact time

The effect of initial concentration on the adsorption of Pb(II) onto DES/H₃PO₄-600 2:3 was examined by varying initial concentrations from 75 to 150 mg/L using adsorbent dosage of 0.2 g. Varying the concentration from 75 to 150 mg/L, the uptake amount of Pb(II) adsorbed increased from 40 to 62.8 mg/g. As observed in Fig. 6, the uptake rate of Pb(II) was concentration dependent and DES/H₃PO₄-600 2:3 had superior removal capacity at the highest concentration investigated. This is because higher concentrations provide the needed driving force that is high enough to repress the mass transfer barrier between DES/H₃PO₄-600 2:3 and the aqueous phase. Similar phenomenon could be observed for adsorption of Pb(II) on potato peels (Kyzas and Mitropoulos 2018). Additionally, the sorption rate of Pb(II) ions was rapid at first 80 min and then becomes almost constant as the removal process proceeds. The sorption rate could be seen to be initially fast at the beginning of the experiment due to the accessibility of large number of sorption sites, but as the reaction proceeds, slower uptake could be observed due to the decrease in available sorption sites on DES/H₃PO₄-600 2:3. Hence, the equilibrium time at 120 min can be considered to be sufficient enough for the removal of Pb(II) by DES/H₃PO₄-600 2:3 from water.

Effect of solution pH on the removal of Pb(II)

pH remains a dominant factor that controls uptake capacity of metal ions from solution(Wang et al. 2011a, b). Figure 7 illustrates the effect of pH on Pb uptake. Increasing the pH values from 1–6, Pb(II) adsorption on to DES/H₃PO₄-600 2:3 increased steadily and attained a maximum peak at a pH value of 5 and afterward deceased. The decrease in sorption rate of Pb(II) at pH < 5 can be traced to the abundant of H⁺ that competes with Pb(II) for the available negative binding sites on DES/H₃PO₄-600 2:3. As the solution pH increased, the DES/H₃PO₄-600 2:3 surface charge increased inversely to pH, which reduces H⁺ competition for available binding sites with Pb(II). Consequently, maximum uptake capacity of DES/H₃PO₄-600 2:3 was 73.5 mg/g, which was reported at initial pH value of 5.0, and could be attributed to electrostatic attraction between the negatively charged surface of the DES/H₃PO₄-600 2:3 and positively charge Pb(II).
As a result of Pb(OH)\(^+\) and/or Pb(OH)\(_2\) (soluble hydroxyl complexes) (initial pH was > 5, the removal efficiency of Pb(II) decreased maximum efficiency by varying initial pH to 5. When the adsorbent dosage = 0.2 g/L, time = 120 min, T = 25 ± 2 °C), where the adsorption isotherms were tested to analyze the sorption behavior. Langmuir (Eq. 1) and Freundlich (Eq. 2) isotherms were described by kinetic equations (Eqs. 6 and 7), respectively, and both the removal rate and removal capacity could be a function of the adsorbent properties (e.g., surface area, porosity, aromaticity, etc.) (Abdallah et al. 2019). Pseudo-first-order model assumes that the removal rate is dependent on adsorption capacity, whereas the pseudo-second-order is controlled by chemisorption (i.e., involves sharing of electron pairs between the adsorbent and adsorbate (Alghamdi et al. 2019). Pseudo-first-order model was used to describe the relationship between equilibrium concentrations of the adsorbate and the adsorption capacity of the adsorbent (Ali et al. 2019). In the present study, Langmuir (Eq. 1) and Freundlich (Eq. 2) isotherms were tested to analyze the sorption behavior of Pb(II) by DES/H\(_3\)PO\(_4\)-600 2:3.

\[
\frac{C_e}{q_e} = \frac{1}{Q_{\text{max}}} b + \frac{C_e}{Q_{\text{max}}} \tag{4}
\]

\[
\ln q_e = \ln K_F + \left( \frac{1}{n} \right) \ln C_e \tag{5}
\]

where \(C_e\) and \(q_e\) are equilibrium concentration of Pb in solution (mg/L) and equilibrium uptake (mg/g), respectively. \(Q_{\text{max}}\) is the maximum/theoretical monolayer adsorption capacity of the adsorbent (mg/g), while \(b\) is related to energy of adsorption. \(n\) and \(K_F\) (mg/g (L/mg)\(^{1/n}\)) are linked to the adsorption capacity and favorability of the removal process, respectively. The Langmuir constants \(Q_{\text{max}}\) and \(b\) were calculated from the slope and intercept of a liner plot of \(C_e/Q_e\) versus \(C_e\) (Fig. 8a), while the Freundlich constants \((n \quad \text{and } K_F)\) were obtained from the slope and intercept of liner plot of \(\ln q_e\) versus \(\ln C_e\) (Fig. 8b). The related parameters of the isotherms are presented in Table 3. Judging on the basis of correlation coefficients \((R^2)\) and \(Q_{\text{max}}\) values, the Langmuir isotherm model revealed more satisfactory results with \(R^2 > 0.9\) as compared to the Freundlich model with \(R^2 < 0.7\), and could be traced to binding sites that are uniformly distributed on DES/H\(_3\)PO\(_4\)-600 2:3. The \(Q_{\text{max}}\) for DES/H\(_3\)PO\(_4\)-600 2:3 was 98.3 mg/g. Compared to other adsorbents, the DES/H\(_3\)PO\(_4\)-600 2:3 demonstrated good adsorption properties. The \(Q_{\text{max}}\) for Pb(II) adsorption was revealed to be 21.38, 49.92, 50.00, 63.29—89.28, 90.0 mg/g from different activated carbons obtained from apricot stone, coconut shell, polypyrrole-based AC, coffee residue AC and municipal organic solid waste, respectively, and in previous studies (Table 2) were below that of DES/H\(_3\)PO\(_4\)-600 2:3. This result revealed that AC prepared by cleaner method using PKS and DES/H\(_3\)PO\(_4\) activating agent is promising, especially for the treatment of Pb in water. The high removal capacity reported by EDS/H\(_3\)PO\(_4\)-600 2:3 could be linked to its ordered pore structure and available function groups on the surface. Equally, maximum adsorption capacity of DES/H\(_3\)PO\(_4\)-600 2:3 was compared to materials with significantly better parameters (Table 2). To quantify the adsorption rate information, the data reported from the kinetic experiment were described by kinetic equations (Eqs. 6 and 7), respectively, and both the removal rate and removal capacity could be a function of the adsorbent properties (e.g., surface area, porosity, aromaticity, etc.) (Abdallah et al. 2019). Pseudo-first-order model assumes that the removal rate is dependent on adsorption capacity, whereas the pseudo-second-order is controlled by chemisorption (i.e., involves sharing of electron pairs between the adsorbent and adsorbate (Alghamdi et al. 2019).

\[
\log(q_e - q_t) = \log q_0 - \frac{k_1 t}{2.303} \tag{6}
\]

\[
t/q_t = 1/k_2 q_e^2 + t/q_e \tag{7}
\]

where \(K_1\) (min\(^{-1}\)) and \(K_2\) (g/mg min) are rate constants for pseudo-first-order and pseudo-second-order, respectively. Also, \(q_t\) and \(q_e\) are the amount of Pb(II) adsorbed per mass of DES/H\(_3\)PO\(_4\)-600 2:3 at any given time \(t\) (min) and at equilibrium, respectively. When \(\log(q_e - q_t)\) vs \(t\) and \(t/q_t\) vs \(q_e\) is plotted, \(K_1\), \(K_2\) and \(q_e\) are obtained from the intercept and slope. The liner equation fitted by kinetic models (pseudo-first- and
pseudo-second-order models) is presented in Fig. 8c-d, and the computed parameters are listed in Table 3. The adsorption process onto DES/H$_3$PO$_4$-600 2:3 followed second-order rate equation. As can be seen from the table, the values calculated from the model showed correlation coefficient ($R^2$) value closer to satisfactory (0.9999) with theoretically calculated $q$ value ($q_{e,cal}$) in good agreement with experimental value ($q_{e,exp}$). These findings indicated that chemisorption mechanism is the rate-limiting step.

![Fig. 8 Adsorption isotherm model of Pb(II) adsorption. a Langmuir; b Freundlich ([Pb]$_o$ = 25, 50, 75, 100 and 125 mg/L); c pseudo-first-order kinetic plot; d pseudo-second-order kinetic plot for the adsorption of Pb(II) ([Pb]$_o$ = 125 mg/L; dosage = 0.2 g/L; time = 140 min; temp. = 25 ± 2 °C)](image)

| Isotherm | Parameters for the adsorption of Pb(II) by DES/H$_3$PO$_4$-600 2:3 according to Isotherm and kinetic models |
|----------|--------------------------------------------------------------------------------------------------|
| Langmuir | $Q_m$ (mg/g) | b (L/mg) | $R_L$ | $R^2$ |
| 97.1     | 0.0481     | 0.1424 | 0.9681 | |
| Freundlich | 1/n (mg/g) | $K_F$ (mg/g)(L/mg)n | $R^2$ |
| 1.2565   | 1.2790     | 0.6565 |

| Kinetics study | Pseudo-first order | Pseudo-second order |
|----------------|-------------------|---------------------|
| $Q_e$ exp (mg/g) | $Q_e$ cal (mg/g) | $k_1$ (min$^{-1}$) | $R^2$ |
| 96.7             | 39.5              | 0.030               | 0.8209 |
| $Q_e$ cal (mg/g) | $K_2$ (g/mg min) | $R^2$              |
| 96.1             | 0.068             | 0.9999             |
Changes in adsorption capacity for the removal process of Pb(II) ions were investigated in the temperature range of 30 to 50 °C. As seen in Fig. 9a, the removal rate for Pb(II) decreased from 90.8 to 54.5 mg/g as the solution temperatures increased. The result demonstrated that the adsorption process of DES/H₃PO₄-600 2:3 for the treatment of Pb(II) in solution is exothermic. Hence, a decrease in solution temperature will be more beneficial to the adsorption of Pb(II). Furthermore, the data obtained from the effect of solution temperature were used to describe the pertinent thermodynamic parameters such as $\Delta G^0$ (Gibbs free energy) (obtained from Eq. 8), $\Delta H^0$ (enthalpy) and $\Delta S^0$ (entropy), both calculated Vant Hoff’s equation (Eq. 9).

\[
\Delta G^0 = -RT \ln K_C \tag{8}
\]

\[
\ln K_C = \left( \frac{\Delta S}{R} \right) - \left( \frac{\Delta H}{R} \right) \frac{1}{T} \tag{9}
\]

$K_C$ is the distribution coefficient, otherwise called the thermodynamic equilibrium constant and was evaluated using.

\[
K_C = \frac{C_a - C_e}{C_e} \tag{10}
\]

where $C_e$ is the amount of Pb(II) on DES/H₃PO₄-600 2:3 (mg/g), $C_a-C_e$ defines the equilibrium concentration of Pb(II) in solution (mg/L), whereas the gas constant is represented by $R$. By increasing solution temperature from 30

**Table 3** Adsorption capacity of various adsorbents compared with DES/H₃PO₄-600 2:3

| Adsorbents           | Activating Agent | $S_{ BET}$ (m²/g) | Total pore volume (cm²/g) | $Q_{max}$ (mg/g) | Reference                                      |
|----------------------|------------------|--------------------|---------------------------|------------------|-----------------------------------------------|
| PKS                  | DES/H₃PO₄        | 1413               | 0.618                     | 97.07            | This study                                    |
| Polypyrrole          | KOH              | 2871               | 0.054                     | 50.00            | Alghamdi et al., 2019                         |
| Apricot stone        | H₂SO₄            | 393                | 0.192                     | 21.38            | Mouni et al., 2011                            |
| Composite            | TiO₂/CF          | 14.95              |                           | 42.5             | Zhang et al., 2016                            |
| Winemaking Waste     | KOH              | 1194               | 1.4                       | 58               | Alguacil et al., 2018                         |
| Coconut shell        | H₃PO₄            | 624                | 0.523                     | 49.92            | Sharaf El-deen & Sharaf El-deen, 2016         |
| Coffee residue       | H₃PO₄            | 1003               | 0.618                     | 89.28            | Boudraham et al., 2011                        |
| Coffee residue AC    | ZnCl₂            | 858                | 0.549                     | 63.29            | Boudraham et al., 2011                        |
| MOSW AC              | H₃PO₄            | 790                | 0.523                     | 90.0             | Al-malack & Basaleh, 2016                     |
| Chickpea husk        | KOH & K₂CO₃      | 2082               | 1.070                     | 135.8            | Özsin et al., 2019                            |
| Milkweed AC          | –                | 170                | 1.07                      | 316.3            | Ilangovan et al., 2017                        |

MOSW = municipal organic solid waste

**Fig. 9** a Adsorption of Pb(II) by DES/H₃PO₄-600 2:3 as a function of temperature, b Vant Hoff’s plot (dosage = 0.2 g/L, time = 140 min, [Pb]₀ = 125 mg/L, pH = 5)
to 50 °C, the $\Delta G^o$ values became less negative ($-1.612$, $-0.858$ and $1.127$ kJ/mol), indicating the spontaneity of the adsorption process of DES/H$_3$PO$_4$-600 2:3 for Pb(II) and its feasibility at lower temperature. At 50 °C, we reported a positive value of $\Delta G^o$, indicating a non-spontaneous process at this temperature. This result is in agreement with the $\Delta H$ ($-43.90$ kJ/mol) confirming the exothermic nature of the adsorption process (Liu et al., 2020), which also supported by the changes in uptake capacity for Pb(II) removal. Equally, the $\Delta S^o$ value was < 0 ($-138.95$ J/Kmol) signifying a decrease in randomness (Liu et al., 2020) at the DES/H$_3$PO$_4$-600 2:3/aqueous interphase in the course of the adsorption process.

**Competitive adsorption**

Single and binary adsorption systems are vital in estimating the efficacy of DES/H$_3$PO$_4$-600 2:3 for Pb(II) removal in wastewater. Heavy metals are known to coexist; their interaction with each other and other components in the water ecosystem has adverse effect on their transport at the solid/aqueous phase interfaces (Park et al. 2016). Consequently, we investigated the adsorption process of DES/H$_3$PO$_4$-600 2:3 for Pb(II) in the presence of Cu(II). By using the removal ratio (i.e., amount adsorbed in bimetal component ($q_e$) to the amount adsorbed in a single component ($Q_m$), we were able to estimate the effect of binary metal solution on the adsorption process of DES/H$_3$PO$_4$-600 2:3. When $Q_e/Q_m > 1$, adsorption is synergistic, when $Q_e/Q_m = 1$, adsorption is non-interactive, and when $Q_e/Q_m < 1$, adsorption is antagonistic. As seen in Fig. 10, the adoption ratio values in the bimetal solution adsorption were < 1 (Pb-Cu = 0.87 and Cu-Pb = 0.66), indicating antagonistic effect of one metal over the other. Pb(II) has shown greater antagonistic effect over Cu(II), with a sorption maxima that is reportedly inversely proportional to the hydrated ionic radii of the metal (Pb(II) = 4.01 Å > Cu(II) 4.19 Å (Chen et al. 2010) and relative positions in the electrochemical series (Abu-nada et al. 2020). These results conform to other studies from Bansode et al. (2003) on pecan shell-based granular activated carbons, Sitko et al. (2013) on graphene oxide, and Xie et al. (2013) on sludge-based AC. However, this trend is contrary to adsorption pattern of Cu > Pb reported by Yantasee et al. (2004) on fine-grained AC functionalized with amine, and Li et al. (2016) on banana peels. This can be attributed to various sorption sites (hydrophobic or nonionic versus ionic) that are less dependent on cation electronegativity on these activated carbons (fine-grained AC functionalized with amine and banana peels) (Bansode et al. 2003) compared to the PKS-based AC investigated in this work.

**Reusability studies**

In order to establish the stability potential and economic viability of DES/H$_3$PO$_4$-600 2:3 in water treatment, a reusability study was conducted using adsorption–desorption experiments in batch mode for three cycles. The preused DES/H$_3$PO$_4$-600 2:3 was agitated for 2 h with 0.1 HNO$_3$ to detach the adsorbed Pb(II) on the surfaces, then ultrasonicated for 15 min and then washed several times with deionized water and dried, before repeatedly used to adsorb Pb(II) from solution. The regenerated result for DES/H$_3$PO$_4$-600 2:3 of 3 cycles is shown in Fig. 11. The result reveals that there was a little reduction in the removal amount from the first to the third cycle compared to the fresh adsorbent by about 7%. The desorption experiments have demonstrated that DES/H$_3$PO$_4$-600 2:3 had potential for efficient remediation of Pb(II) in water and a probably renewable adsorbent.

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**Fig. 10** Adorption of Pb(II) by DES/H$_3$PO$_4$-600 2:3 as function of the co-cations in solution (Time = 120 min, pH = 5, Temp. = 25 ± 2 °C)

**Fig. 11** Effect of regeneration of DES/H$_3$PO$_4$-600 2:3 on adsorption capacity
Real wastewater treatment

The chemical composition of an effluent from an industrial discharge may differ largely to the synthetic wastewater. As an appraisal of the results of the present study for application to a real wastewater treatment, the use of an industrial wastewater sample was proposed. For this purpose, wastewater collected from an industrial plant was investigated. The wastewater sample, which contained up to 81.0 mg/L, was treated using DES/H₃PO₄-600 2:3. The result from the analysis of the effluent using atomic adsorption spectrometer showed that DES/H₃PO₄-600 2:3 was capable to reducing the amount of Pb(II) in the effluent to below 0.5 mg/L, though, above 100 min of treatment, the concentration of Pb(II) in the effluent was lower than the detection limit of the instrument. The result has demonstrated that DES/H₃PO₄-600 2:3 is a promising alternative for the treatment of Pb(II) from real wastewater. The removal profile for the treatment of Pb(II) from the effluent using DES/H₃PO₄-600 2:3 is shown in Fig. 12.

Conclusions

We have demonstrated a new approach in the preparation of a low-cost AC, using inexpensive PKS and eco-friendly DES/H₃PO₄, for a high efficient adsorbent with a green chemical framework for the treatment of Pb in water. The EDS/H₃PO₄-600 2:3 showed good porous structure and large surface area (1413 m²/g), resulting in satisfactory adsorption of Pb(II). The XPS and FTIR characterization revealed the oxygen-containing groups on EDS/H₃PO₄-600 2:3 due to activation of DES/H₃PO₄ which played a vital role in the removal Pb(II) ions. The result indicated that increasing the initial concentration and the pH value increases the amount removal. The adsorption test was well described by Langmuir model and pseudo-second-order kinetic equation. Meanwhile, increasing the solution temperature decreased the adsorption capacity of the prepared DES/H₃PO₄-600 2:3. The negative value of the enthalpy ΔH (−43.90 kJ/mol) showed that the adsorption process of Pb(II) on DES/H₃PO₄-600 2:3 was exothermic and spontaneous under the condition investigated.

The novelty of this work is that applying DES/H₃PO₄ as an activating agent gives a good ordered activated carbon structure that has significantly promoted adsorption and offers a practical benign/cleaner production approach in the synthesis of activated carbon with good reusability and good wastewater purification ability. To ensure process sustainability, future studies will be focused on long-term pilot studies using column for potential scale-up and revealing the competitive effect of other metals on Pb removal in column.

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Declarations

Conflicts of interest  The authors declare that they have no conflict of interest.

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