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Research Article

Keywords: PANI, Kieselguhr, Hybrid material, Adsorption, Bisphenol A.

Posted Date: November 8th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1036863/v1

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Synthesis, characterization and adsorption of Bisphenol A using novel hybrid material produced from PANI matrix reinforced by Kieselguhr

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Abstract

This study investigated the preparation of new adsorbent based PANI and Kieselguhr (KG). The produced materials were characterized by XRD, XPS, TEM, FTIR, TGA and BET. Thereby, hybrid material PANI@KG highest $S_{BET}$ values (about $47.82 \, \text{m}^2\,\text{g}^{-1}$). The adsorption capacity of the PANI, KG and PANI@KG were tested on BPA ions from aqueous solutions at ambient temperature and pH 6.0, the maximum capacity of adsorption was observed to be 63.68 mg·g$^{-1}$ which is obtained from Langmuir adsorption isotherm by hybrid adsorbent PANI@KG. Besides, the pseudo-2nd order kinetics was more consistent with the obtained experimental data. Furthermore, the hybrid material possessed highest adsorption capacity after six cycles of adsorption-desorption process. Moreover above 80% of removal percentage was obtained even after three recycles. Hence we expect that this organic-inorganic adsorbent can be selected as a potential candidate for water treatment.

Keywords: PANI; Kieselguhr; Hybrid material; Adsorption; Bisphenol A.
1. Introduction

Certain phenolic components are some of the most contaminating and serious organic chemicals even at their low concentration for the destroyed effect against human health [1]. So the elimination of those products from wastewater is defiance for researchers. Among all, Bisphenol A (BPA), one of phenolic materials consisting two aromatic rings and two hydroxyl groups, is applied in the production of epoxy resin and polycarbonate [2, 3], and can also be applied as an additive in flame retardants, plasticizers, antioxidants, etc. [4, 5]. Moreover, BPA is acceptably soluble in water at 298K, and its occurrence in water come mainly from chemical industrials activity and wastewater treatment facilities [6, 7]. Thus, developing of novel ways for efficient removal of BPA from the aqueous solution is highly desirable, e.g. oxidation method [8], electrochemical oxidation [9], membrane filtration [10], reverse osmosis [11], chemical coagulation [12], photocatalysis [13], biological methods [14], adsorption method [1, 3], etc, in which the adsorption is the simple and most effective.

Kieselguhr (KG) or diatomaceous earth is categorized as non-crystalline conforming to the mineralogical class. KG usually consists about 90% SiO$_2$, with significant quantity of Al$_2$O$_3$ and Fe$_2$O$_3$ and some other impurity. KG can be facilely produced at a low cost because diatomaceous silica is the most abundant form of silica on the earth [15-18]. Highly sorption ability, perfect porous structure, chemical stability, accepted surface area, low density are some unique proprieties of KG [19]. Due to these exceptional characteristics KG be used in many several applications such as adsorbent, filter aid, catalyst supports or carrier, insulating materials, natural insecticides, and etc [20, 21].
Among the conducting polymers, PANI is one of the most popular due to its simple preparation, high redox stability, and high capacitance, low cost and eco-friendly performance [22-25]. It is selected as an active material from the viewpoint of technological application-oriented and scientific research, owing to its ease of synthesis, wide variety, and efficiency [25, 26]. It has been described that it is exceedingly employed in combination with hybrid materials to ameliorate properties, such as PANI/Diatomite [27], Fibrillar polyaniline/diatomite [28], PANI-doped tin oxide-diatomite [29] and mDE@PANI [30].

The particular of our present work is that a adsorbent PANI@KG was prepared through polymerization of aniline in the dispersed system of KG, and was characterized via different ways, including XPS, FT-IR, XRD, TGA, TEM and BET. The adsorption kinetics and equilibrium isotherms for BPA removal has been examined with variation in process parameters, e.g. BPA concentration, Influence of pH, contact time, isotherm and regeneration.

2. Experimental

2.1. Materials

Aniline (ANI) (Aldrich, ≥99.5% purity), Bisphenol A (BPA) (Aldrich, ≥99% purity), Kieselguhr (KG) (ENOF, Algeria), Ammonium persulfate (APS) (Merck, ≥98% purity), Ammonia solution (NH₄OH) (Merck, 25% purity), Perchloric acid (HClO₄, Merck, 70% purity), Hydrochloric acid (HCl, Merck, 37%), Ethanol (C₂H₅OH) (Merck, 96% purity) and the ultrapure H₂O (18.2 MΩ.cm) employed in all experiments were obtained from an Elga-Labwater-Purelab system.

2.2. Measurements
X-ray photoelectron spectroscopy (XPS) was recorded using (VGMicrotech Multilab-3000Electron). X-ray diffraction patterns of all the samples were attained on Bruker-CCD-Apex instrument in 20 range of 0.2°–70° at a scan rate of 10° min^{-1} using Cu-Kα X-ray radiation source. Fourier transform infrared spectrum (FTIR) was carried out by Bruker-Inc., Model-Alpha spectrometer between 400–4000 cm\(^{-1}\). The morphologies on their surface were investigated by using transmission electron microscopy (TEM) (JEOL-JEM-2010). UV-Vis spectra (Hitachi_U3000-Spectrophotometer) were tested to calculate the BPA concentrations. Thermogravimetric analysis (TGA) (Hitachi-STA 7200Instrument) was applied to define the thermal stability of adsorbents. The BET isotherms of the materials were obtained from a Autosorb-6-Quantachrome system at liquid N\(_2\) temperature (77 K). Correspondingly, N\(_2\) adsorption is fundamentally to gain the data on total micropore volume (V\(_{DR}\)) using the Dubinin Radushkevich (DR) law and to calculate the specific surface area according to BET equation (S\(_{BET}\)) [21, 22].

### 2.3. Adsorbents preparation

Solutions were prepared by adding 10 g of KG compound to 500 ml of HCl (1M) followed by continuous stirring for ½ h. About 1.35 g of ANI was then added to each previous solution with continuous stirring for 24 h. The polymerization process is carried out at room temperature by APS as oxidizing agent (applied 1:1 APS/ANI mole ratio) following the reported procedure [28-32]. The obtained PANI@KG material were vacuum dried at 65°C for 4 h to be ready for further characterizations. The PANI was prepared in same method above-mentioned but in without presence of KG.

### 2.4. Batch adsorption experiments for removal of BPA
The batch adsorption experiments are conducted for the effective elimination of BPA by the synthesized materials. A known amount of adsorbent along with 25 mL of test solution containing BPA were taken in pyrex bottles and agitated in an orbital shaker for 4 hours to reach equilibrium. After agitation, the absorbent was removed and the concentration of BPA in the filtrate was analyzed using UV-vis.

On account of finding the adsorption capacity of the adsorbent, the uptake of BPA by unit gram of adsorbent is calculated using the following equation [31],

\[ Q_{eq} = \frac{(C_0 - C_{eq})V}{m} \]

where \( C_0 \) is the initial BPA concentration and \( C_{eq} \) represents the equilibrium concentration of BPA, \( Q_{eq} \text{ (mg.g}^{-1}) \) denotes the adsorption capacity, \( V \) being the volume of BPA solution (L), and \( m \) indicates the adsorbent dosage (g).

3. Results and Discussion

3.1. Physicochemical characterization

XPS was carried out to further analyze the chemical composition of the synthetized materials. Fig. 1-a. show the XPS wide survey spectrum of KG material give the characteristic peaks of Si2p3, Si2p1, Ca2p3, Ca2p1, Fe2p and O1s with the assigned binding energies of 102.70 eV, 103.43 eV, 347.82 eV, 350.95 eV, 710.59 eV and 531 eV, respectively. Furthermore, the binding energy values of the principal peaks (Si2p, O1s, C1s and N1s) in the investigated PANI@KG are reported in Table 1, and Cl1s peak at 200.15 eV displays the presence of chlorine (Cl). The Cl peak exhibits that HClO\(_4\) added over at synthesis reaction, together with the signals of C and N elements can be clearly observed in PANI chain.
Fig. 2-a. displays the high resolution C1s spectra of PANI. We can see that four kinds of peaks centered at 284.56 eV (C–H/C=C/C=O), 285.66 eV (C–O), 286.94 eV (C–O) and 290.96 eV (O=C=O). These functional groups mentioned are in approval with other work. [21, 22].

Similarly, the same peaks attributed to PANI were displayed in the C1s spectrum of PANI@KG and the content of the O=C=O group were disappeared (Fig. 2-b), supporting the reaction between PANI and KG. The high-resolution XPS spectra are summarized in Table 1.

Moreover, The N1s spectra of PANI consist of three broad peaks, at 399.45 eV, 400.62 eV and 401.83 eV shows the presence of quinoid phenyl structure (−N=), benzenoid structure (−NH−) and quaternary ammonium salt structure (N+), respectively. Likewise, after the deconvolution, N1s of PANI@KG presents three peaks at 399.47 eV, 400.68 eV and 402.16 eV assigned to (−N=), (−NH−) and (N+) respectively, as exhibit in Fig. 2-(c,d). It may be mentioned that N1s spectra is moved to higher binding energies value indicating the modification electronic charge of nitrogen.

In Fig. 1-b. the XRD pattern reveals the presence of an amorphous phase (opaline silica, SiO$_2$·nH$_2$O) with the characteristic broad peak centered at 22.62°, and a single sharp peak at 2θ = 26.26° corresponding to amorphous SiO$_2$ with small amount of quartz [32]. Moreover, the amorphous character of pure PANI is indicated by the hump-like peak at 2θ range 10-35° [33]. The XRD pattern of PANI@KG revealed mixed phases, it because a change in their peak positions and shapes compared with the pure PANI and KG indicating that either the KG was successfully incorporated into the PANI matrix or the KG were dispersed well on the surface of the PANI chain.

FTIR spectroscopy was carried out to analyze the surface characteristics of PANI, KG and PANI@KG samples. In Fig. 3. the spectrum of KG confirms the presence of CO$_3^{2−}$
deformation bands at 1441 cm\(^{-1}\) and 870 cm\(^{-1}\) from calcite and ankerite in KG [34]. The bands at
870 cm\(^{-1}\) and 1441 cm\(^{-1}\) assured the existence of calcite in KG. As display in Fig. 3.a, the
absorption band at 1069 cm\(^{-1}\) was associated to asymmetrical stretching vibrational modes of
siloxane (Si–O–Si) [35]. The band at 793 cm\(^{-1}\) was associated to Al–O–Si stretching vibration
related to the clays in KG [36]. Moreover, typical bands of PANI were found at 1516 cm\(^{-1}\) and
1451 cm\(^{-1}\) are attributed with the benzene ring stretching of C=C–C bonds. These bands that
are called as stretching vibrations of N=Q=N and N–B–N (Q = quinoid and B = benzoid) are in
perfect agreement with those reported other work [26]. The bands at 1322 cm\(^{-1}\) and 1208 cm\(^{-1}\)
are due to C–N bend vibration, in groupings of the systems B and Q. Furthermore, the band at
806 cm\(^{-1}\) corresponds to −C−N out of plane bending vibrations of C−H in the benzene ring.
Around 3271 cm\(^{-1}\), it was observed an absorption band for N–H stretching of the amine group.
In addition, the most changes resulting in PANI@KG was the appearance of the three bands at
1320 cm\(^{-1}\), 1441 cm\(^{-1}\) and 1504 cm\(^{-1}\) attributed to the vibration of C–N, CO\(_3^{2−}\) and C=C–C,
respectively. The stretching vibration of Si–O–Si showing a displacement to 1063 cm\(^{-1}\)
compared with that of KG which confirms that the synthesized product was indeed PANI@KG.
The surface areas and also pore size distributions of samples were investigated by the
Brunauer–Emmett–Teller (BET) method (Fig. 4-a). All the materials exhibited the isotherm of
type III and similar H\(_3\) hysteresis loop. The obtained BET surface areas of PANI, KG and
PANI@KG are found to be 7.6 m\(^2\).g\(^{-1}\), 12.9 m\(^2\).g\(^{-1}\) and 22.9 m\(^2\).g\(^{-1}\) respectively. The BET
areas, total pores and mesoporous volumes of adsorbents are provided in Table 2. The surface
area is greater for PANI@KG compared to PANI and KG which shows the presence of more
surface active sites for adsorption [37].
Fig. 4-b. shows the TGA curves of the samples. PANI@KG presented the initial weight loss (1.14%) below 295°C, which was associated to loss of H$_2$O and solvent molecule. The second weight loss (4.22%) in range between 295°C and 372°C was attributed to breaking chemical bonds of polymer chain from their frameworks. At 900°C, the global amount loss of nanocomposite was 21.43%, while polymer was 67.82%. The cause is that the existence of KG on polymer matrix promoted the growth of the crystal [38]. It was determined that PANI@KG had preferable thermal stability than pure PANI.

The PANI@KG was characterized through (TEM) in order to analyze the surface morphology and compare it to the KG and PANI as in Fig. 5. TEM image of nanocomposite exhibit that KG is homogenously dispersed and these particles are surrounded by polymer matrix with less degree of aggregations which confirms the crystallinity of the PANI@KG. Moreover, the KG shows obvious lattice fringes. While PANI shows a classically morphology and much dark structure with homogenous distribution [22-25]. Moreover, the elemental chemical composition (wt%) of the PANI@KG nanocomposite used in this study was: C: 11.79; O: 26.84; Si: 31.51; Na: 4.21; Mg: 2.54; Al: 12.15; S: 1.59; K: 2.98 and Fe: 6.48. The chemical compositions of PANI and KG are reported in Table 3.

3.2. Adsorption of BPA

3.2.1. Influence of pH

The optimized solution’s pH is a key factor to maximize the organic pollutants removal on the used adsorbent surface since the solution’s pH influence various factors in the elimination method including a surface charge of the adsorbent, organic ion distribution, and dissociation rate of the functional group found on adsorbent active sites. The removal process
was investigated under various solutions’ pH in range of 2 to 12. The influence of pH on the adsorbed BPA amount are displayed in Fig. 6-a. As it is clear, when pH increased to 6.0, the removal capacity of KG to BPA rose. This is because BPA commences to partly dissociated, and BPA BPA is no longer on molecular form in the solution, but part of monoanions (HBPA$^-$) shows. The KG surface is positively charged, and the electrostatic attractions between this adsorbent and HBPA$^-$ fosters the removal. The after increase in pH produced in decrease in the removal capacity of adsorbents to BPA. This is because the $\pi$$-$$\pi$ electron donor/acceptor interaction and H-bonding between adsorbent and BPA is little when the solution pH is superior to the pK$_a$ of BPA [39]. Moreover, the removal capacity of BPA by PANI@KG increased at initial and then reduced with the rises of pH, and the maximum removal capacity occurred near pH 6.0. With the increase of pH, also the dissociation of BPA increases. The augmentation in HBPA$^-$ leads to boosted electrostatic attraction between BPA and PANI@KG. When the pH continues to increase, BPA also dissociates to produce the more negative dianion (BPA$^{2-}$), which produces repulsion with the surface of PANI@KG, lead to diminution in the removal capacity [40]. Meanwhile, the elimination of BPA by PANI was the high when the pH was weak i.e. from 2.0 to 6.0, with small differences. A limited in BPA elimination was detected as the solution pH was augmented from pH 6.0 to 12.0. This remark was attributed to the hypothesis that, in alkaline condition, a negative charged is formed on the PANI surfaces, and correspondingly, the $-\text{OH}$ functions become deprotonated to form HBPA$^-$ and BPA$^{2-}$. This resulted in repulsion between the PANI chain and BPA ions.

3.2.2. Effect of adsorption time

Contact time is another important building block to get the maximum BPA ion removal by the materials adsorbents. Fig. 6-b. Percentage removal of the BPA ions at various time
intervals were studied by using 1g/25mL adsorbent for a concentration of 500 mg.L$^{-1}$ at a pH of 6.0 and at 25°C. As can be seen, all specimens showed similar trends. As time goes, BPA ion removal increases speedy to reach an optimum time point attributed to the presence of the vacant sites on the adsorbents surfaces. Then, the adsorption ratio remains nearly constant due to saturated of the adsorbents active sites. Moreover, the figure confirms that the maximum adsorption of the selected BPA ions on the prepared adsorbents could be obtained by adopting a 120 min contact time. As it was discussed, increasing the contact time did not result in the BPA ion adsorption increase, on adsorbents surface.

### 3.2.3. Adsorption kinetics

Adsorption kinetics of BPA ions on three adsorbents was analyzed by employing pseudo-first-order (PFO) and pseudo-second-order (PSO) models. The kinetics was studied for the adsorption of BPA ions having the initial concentration of 500 mg.L$^{-1}$.

The PFO kinetics describes the adsorption occurring between solid/liquid systems depending upon the removal capability of adsorbents [41]. The linear equation for PSO kinetics is equated as follows [42]:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} - \frac{k_1}{2.303}t$$

Where, $Q_e$ and $Q_t$ are the equilibrium concentration and concentration at time $t$ of BPA (mg.g$^{-1}$) respectively and $k_1$ being the PFO rate constant (min$^{-1}$) of adsorption. The PFO linear fitting plot of $log(Q_e - Q_t)$ vs $t$ gives a poor correlation coefficient (Table 3) showing that the first order kinetic model was not followed by the adsorption process.
The PSO kinetics formula explains a chemisorption phenomenon from solution [43].

The linear equation is written as follows:

\[
\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}t
\]

where, \(k_2\) denotes the PSO rate constant (g.mg\(^{-1}\).min), \(Q_e\) and \(Q_t\) represents the adsorption capacities (mg.g\(^{-1}\)) at equilibrium and time \(t\) respectively and \(k_2Q_e^2\) is the initial adsorption rate (g.mg\(^{-1}\).min).

The PSO model better the best-fitting to the obtained data compared by PFO model. Therefore, the FSO model is more adequate for interpreting the kinetics of the select BPA on the three adsorbents and substantiates the adsorption to be chemisorption involving electronic forces through sharing or exchange of electrons between the adsorbent and ionized species as a function of electron donor or acceptor, respectively, regardless of equilibrium concentrations [44]. According to \(R^2\) constant values presented in Table 4. Besides, the determined value of \(Q_{eq,Cal}\) acquired from PSO type is nearer to experiential values of \(Q_{eq,Exp}\).

### 3.3. Adsorption isotherms of BPA

The adsorption isotherm gives the amount of BPA adsorbed by adsorbent materials at a fixed temperature in Fig. 6-c. The Freundlich and Langmuir isotherms have been adopted to fit the experimental values.

The Langmuir isotherm explains the adsorbent surface to be uniform containing fixed number of adsorption sites and also the adsorption is monolayer. The linear equation for Langmuir isotherm can be written as follows [45]:
\[
\frac{c_{eq}}{Q_{eq}} = \frac{1}{K_l C_m} + \frac{c_{eq}}{Q_m}
\]

Where \(Q_{eq}\) is the amount adsorbed (mg.g\(^{-1}\)), \(C_{eq}\) is the equilibrium concentration of the adsorbate (mg.L\(^{-1}\)), \(K_l\) (L.mg\(^{-1}\)) are Langmuir constants and \(Q_m\) (mg.g\(^{-1}\)) is the maximum adsorption capacity of adsorbent.

Both physisorption (multilayer) and chemisorption (monolayer) can be determined applied the Freundlich isotherm. This type is based on the heterogeneous equilibrium on adsorbent surface. The equation for Freundlich isotherm is as follows [46]:

\[
\ln Q_{eq} = \ln K_f + \frac{1}{n} \ln C_{eq}
\]

where \(K_f\) (mg\(^{1-1/n}\).L\(^{1/n}\).g\(^{-1}\)) and \(n\) are the Freundlich isotherm constants which refers to capacity and intensity of adsorption, respectively, and \(C_{eq}\) is referred as equilibrium concentration (mg.L\(^{-1}\)).

The matching result of adsorption isotherm applied Langmuir and Freundlich types are summarized in Table 5. Several investigators suppose that \(n\) displays a high affinity between adsorbate and adsorbent and also the appearance of chemisorption when major than unities [47]. Since the correlation coefficient (\(R^2\)) are found to be 0.977, 0.961 and 0.991correspond to KG, PANI and PANI@KG adsorbents, respectively. The adsorption results of BPA fit well with Freundlich isotherm. Furthermore, one possible cause for the preferable performance of the formed PANI@KG adsorbent is the elimination mechanism, which appears in both anion exchanges on adsorbents surface by hydrogen-bonding with \(\pi-\pi\) liaisons. A comparison of relative adsorption using different adsorbent materials using literature has been summarized in table 6 [48-56].
3.4. Adsorption mechanism

The presence of polymer matrix on KG surface reasons the surface to be negatively charged which play a significant role in this adsorption process. The removal mechanism can be clarified in two methods. Physisorption can be produced on PANI surface or in KG porosity or chemisorption by interaction between PANI and BPA ions. Therefore, the surface area determined from BET analysis plays a substantial role in the electrostatic attraction process thereby favouring the effective removal process. From BET analysis, the surface area of PANI@KG is greater than PANI and KG thereby indicating that hybrid material exhibits more excellent adsorption performance for BPA than others. Moreover, the presence of quinone and benzene groups with delocalized π-conjugated structures and electrochemically active sites in the PANI matrix forming an additional agent on the KG surface and enhance the favorable adsorption of BPA ions.

3.5. Reuse of adsorbent

The reusability has been studied in a qualitative manner for three adsorbent materials since the reusability may be crucially important parameter for keeping the process cost down and reduce waste. After desorption process, the adsorbent was washed repeatedly several times with C\textsubscript{2}H\textsubscript{5}OH and distilled H\textsubscript{2}O. The reusability results are present in Fig. 6-d. The PANI showed decreasing in the adsorption capacity after six cycles of adsorption-desorption process under optimized conditions of pH 6.0, 1g/25mL of adsorbent dosage and initial BPA concentration of 500 mg.L\textsuperscript{-1}. On the other hand, the adsorption capacity of the KG material decreased from 21.53% to 7.03% after also six cycles. However, in the PANI@KG still possessed better adsorption capacity than PANI and KG after five cycles. Besides, the removal
efficiency was higher than 80% even after three cycles indicating that the synthesized hybrid material acts as an effective adsorbent in the removal of BPA.

4. Conclusions

This study investigated the preparation of new adsorbent based PANI and KG. The characterizations of the materials obtained were carried out by XPS, XRD, FTIR, TGA, SEM and N$_2$ adsorption-desorption isotherms. The adsorption capacity of the PANI, KG and PANI@KG were tested on BPA ions from aqueous solutions at 298 K and pH 6.0 and the maximum capacity of adsorption was observed to be 63.68 mg.g$^{-1}$ which is obtained from Langmuir adsorption isotherm by hybrid adsorbent PANI@KG. Besides, the PSO was more consistent with the obtained experimental data. The type of adsorption is found to chemisorption from the kinetic measurements. Further, the PANI@KG possessed highest adsorption capacity after six cycles of adsorption-desorption process. Moreover above 80% of removal percentage was obtained even after three recycles. Hence we expect that this organic-inorganic hybrid can be selected as a potential candidate for water treatment.

Acknowledgements

Authors gratefully acknowledge the Algerian MESRS and also Instituto Universitario de Materiales of Alicante University (Spain) for the co-operation availing.

Funding information: There is no financial sources funding regarding of this study.

Declaration of Competing Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this manuscript.
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Captions

**Fig. 1.** (a) Survey XPS spectra and (b) XRD patterns of KG, PANI and PANI@KG.

**Fig. 2.** XPS core-level spectra of (a) C1s of PANI, (b) C1s of PANI@KG, (c) N1s of PANI and (d) N1s of PANI@KG.

**Fig. 3.** FTIR spectrum of KG, PANI and PANI@KG.

**Fig. 4.** (b) BET surface area and (c) TGA curves of materials

**Fig. 5.** TEM images of: (a) KG; (b) PANI and (c) PANI@KG.

**Fig. 6.** (a) Effect of pHs on the adsorption capacity, (b) Contact Time \(C_0: 500 \text{ mg.L}^{-1}; \text{pH: 6.0}; T: 298K; \text{adsorbent dose: 1g}\), (c) Adsorption isotherms \(\text{adsorbent dose: 1g; BPA 25 mL; T: 298 K; pH: 6.0}\) and (d) Adsorbent capacity change and first BPA in consecutive cycles \(\text{adsorbents dose: 1g; BPA: 25mL; T: 298K; pH 6.0}\).
Table 1. XPS values of Binding Energy (BE) for: (A) PANI, (B) KG and (C) PANI@KG materials.

| Species | Materials and BE (eV) | Remarks                  |
|---------|-----------------------|--------------------------|
|         | (A) | (B) | (C)               |                  |
| Si2p3   | //  | 102.70 | 102.97 | Si\(^{4+}\) in SiO\(_2\) |
| Si2p1   | //  | 103.43 | 103.50 |                  |
| Ca2p3   | //  | 347.82 | //     | Ca\(^{2+}\) ions |
| Ca2p1   | //  | 350.95 | //     |                  |
| Fe2p    | //  | 710.59 | //     | Fe\(^{2+}\) ions |
| O1s     | 531.35 | 531.06 | 531.42 | C=O, O=C–OH       |
|         | 532.50 | 532.41 | //     | Si–O–Si, C–OH     |
|         | 533.74 | //     | 533.29 | Si–O–C, Zn–OH, H\(_2\)O |
| C1s     | 284.56 | 284.86 | 284.29 | C–H, C–C, C=C     |
|         | 285.66 | //     | 285.64 | C–N               |
|         | 286.94 | //     | 287.32 | C–O               |
|         | 290.96 | //     | //     | O–C=O             |
| N1s     | 399.45 | //     | 399.47 | =N–                |
|         | 400.62 | //     | 400.68 | –NH–              |
|         | 401.83 | //     | 402.16 | N\(^+\)           |
| Cl2p    | 199.97 | 200.08 | 200.15 | Cl ions           |

Table 2. Textural properties of materials.

| Materials | BET area \(S_{\text{BET}}\) m\(^2\).g\(^{-1}\) | Total pores volume \(V_t\) cm\(^3\).g\(^{-1}\) | Mesoporous volume \(V_{\text{mes}}\) cm\(^3\).g\(^{-1}\) |
|-----------|----------------------------------|----------------------------------|----------------------------------|
| PANI      | 36.58                            | 0.174                            | 0.087                            |
| KG        | 6.47                             | 0.029                            | 0.027                            |
| PANI@KG   | 47.82                            | 0.179                            | 0.059                            |

Table 3. Chemical composition (wt\%) of samples.

| Weight % | C   | Si  | O   | S   | Na  | Mg  | Al  | Ca  | K   | Fe  | Cl  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| KG       | //  | 47.22 | 29.18 | //  | //  | 2.47 | 8.17 | 6.86 | 0.21 | 5.66 | 0.23 |
| PANI     | 63.21 | 0.79 | 20.70 | 3.38 | 9.88 | //  | //  | //  | //  | 3.04 |     |
| PANI@KG  | 11.79 | 31.51 | 26.84 | 1.59 | 4.21 | 2.54 | 12.15 | //  | 2.98 | 6.36 | 0.12 |
Table 4. PFO and PSO removal rate constant and $Q_{eq}$ value for elimination of BPA by nanoadsorbents at 298 K, pH 6.0 and $C_0$ 500 mg L$^{-1}$.

| Materials   | $Q_{eq,Exp} \text{ (mg.g}^{-1})$ | PFO      | PSO      |
|-------------|----------------------------------|----------|----------|
|             | $k_1 \text{ (min}^{-1})$       | $Q_{eq,Cal} \text{ (mg.g}^{-1})$ | $R^2$    | $k_{2,ads} \text{ (g.mg}^{-1}.\text{min}^{-1})$ | $Q_{eq,Cal} \text{ (mg.g}^{-1})$ | $R^2$    |
| PANI        | 37.43                           | 0.009    | 58.11    | 0.912    | 0.0003           | 35.86    | 0.992    |
| KG          | 14.92                           | 0.003    | 28.58    | 0.923    | 0.0014           | 16.38    | 0.997    |
| PANI@KG     | 63.68                           | 0.416    | 69.65    | 0.907    | 0.0010           | 62.92    | 0.996    |

Table 5. Langmuir & Freundlich isotherms constant and correlation coefficient for removal of BPA on adsorbents at 298K and pH 6.0.

| Adsorbents | Langmuir | Freundlich |
|------------|----------|------------|
|            | $Q_m \text{ (mg.g}^{-1})$ | $K_L \text{ (L.mg}^{-1})$ | $R_L$ | $R^2$ | $K_F \text{ (mg}^{-1/1-n_L} \text{L}^{1/n} \text{g}^{-1})$ | $n$ | $R^2$ |
| PANI       | 22.93    | 0.114      | 0.275   | 0.846 | 2.477           | 1.95    | 0.977    |
| KG         | 6.37     | 1.097      | 0.125   | 0.908 | 4.017           | 4.37    | 0.961    |
| PANI@KG    | 56.81    | 0.080      | 0.180   | 0.699 | 8.678           | 2.35    | 0.991    |
Table 6. Adsorption capacities ($Q_{eq}$) of BPA on various adsorbents.

| Adsorbents                                  | $Q_{eq}$ (mg.g$^{-1}$) | pH  | Ref.   |
|---------------------------------------------|------------------------|-----|--------|
| Synthesized chitosan                        | 34.00                  | 5.0 | [48]   |
| Activated carbon                            | 41.00                  | 5.0 | [49]   |
| Sugi chip                                   | 11.50                  | 7.0 | [50]   |
| Modified fibric peat                         | 29.15                  | //  | [51]   |
| Composited modified bentonite CPAB/EGIS/B    | 119                    | 7.0 | [52]   |
| CPAB/B                                      | 27.87                  | 7.0 | [52]   |
| EGIS/B                                      | 97.52                  | 7.0 | [52]   |
| Fe$_3$O$_4$@polyaniline core–shell          | 9.13                   | 7.0 | [53]   |
| Graphene oxide incorporated Fe$_3$O$_4$@polyaniline | 14.43                | 6.0 | [54]   |
| Fe$_3$O$_4$@SiO$_2$@polyaniline graphene oxide | 454.56              | 6.0 | [55]   |
| Magnetic Multiwalled Carbon Nanotube         | 21.43                  | //  | [56]   |
| PANI@KG                                     | 63.68                  | 6.0 | This work |

This work
Figures

(a) Survey XPS spectra and (b) XRD patterns of KG, PANI and PANI@KG.

Figure 1

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