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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_2O_3 and Fe_2O_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, $\geq 99.5\%$ purity), Bisphenol A (BPA) (Aldrich, $\geq 99\%$ purity), Kieselguhr (KG) (ENOF, Algeria), Ammonium persulfate (APS) (Merck, $\geq 98\%$ purity), Ammonia solution (NH_4OH) (Merck, 25% purity), Perchloric acid (HClO_4 , Merck, 70% purity), Hydrochloric acid (HCl , Merck, 37%), Ethanol ($\text{C}_2\text{H}_5\text{OH}$) (Merck, 96% purity) and the ultrapure H_2O (18.2 $\text{M}\Omega\cdot\text{cm}$) 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 2θ range of 0.2° – 70° at a scan rate of $10^\circ \text{ min}^{-1}$ using Cu-K_α 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 $\frac{1}{2} \text{ h}$. 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 adsorbent 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} (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 synthesized 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 HClO₄ 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=C), 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, SiO₂·nH₂O) with the characteristic broad peak centered at 22.62°, and a single sharp peak at 2θ = 26.26° corresponding to amorphous SiO₂ 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 CO₃²⁻

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 $7.6\text{ m}^2.\text{g}^{-1}$, $12.9\text{ m}^2.\text{g}^{-1}$ and $22.9\text{ m}^2.\text{g}^{-1}$ 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 H₂O 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 is no longer on molecular form in the solution, but part of monoanions (HBPA^-) shows. The KG surface is positively charge, and the electrostatic attractions betwixt 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 π - π 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 product 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]:

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

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:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$$

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

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 ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$) 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 0.991 correspond 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 π - π 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_2H_5OH and distilled H_2O . 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^{-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 N₂ 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.

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References

- [1] S.A. Hoshyar, H.A.H. Barzani, Y. Yardım Z. Şentürk. The effect of CTAB, a cationic surfactant, on the adsorption ability of the boron-doped diamond electrode: Application for voltammetric sensing of Bisphenol A and Hydroquinone in water samples. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 610 (2021) 125916.
- [2] M.V.L. Ramón, R.O. Pérez, M.I.B. Toledo, J.R. Utrilla, C.M. Castilla, M.S. Polo. Removal of bisphenols A and S by adsorption on activated carbon clothes enhanced by the presence of bacteria. *Science of the Total Environment*. 669 (2019) 767-776.
- [3] X. Men, Q. Guo, B. Meng, S. Ren, B. Shen. Adsorption of bisphenol A in aqueous solution by composite bentonite with organic moiety. *Microporous and Mesoporous Materials*. 308 (2020) 110450.
- [4] R. Rezg, S. El-Fazaa, N. Gharbi, B. Mornagui. Bisphenol A and human chronic diseases: current evidences, possible mechanisms, and future perspectives. *Environment International*. 64 (2014) 83-90.
- [5] Y.Q. Huang, C.K.C. Wong, J.S. Zheng, H. Bouwman, R. Barra, B. Wahlström, L. Neretin, M.H. Wong. Bisphenol A (BPA) in China: a review of sources, environmental levels, and potential human health impacts. *Environment International*. 42 (2012) 91-99
- [6] A. Careghini, A.F. Mastorgio, S. Saponaro, E. Sezenna. Bisphenol A, nonylphenols, benzophenones, and benzotriazoles in soils, groundwater, surface water, sediments, and food: a review. *Environmental Science and Pollution Research*. 22 (2015) 5711-5741.

- 340 [7] D.C. Arriagada. Elucidating the co-transport of bisphenol A with polyethylene terephthalate
 341 (PET) nanoplastics: A theoretical study of the adsorption mechanism. *Environmental*
 342 *Pollution*. 270 (2021) 116192
- 343 [8] J. Sharma, I.M. Mishra, V. Kumar. Degradation and mineralization of Bisphenol A (BPA)
 344 in aqueous solution using advanced oxidation processes: UV/H₂O₂ and UV/S₂O₈²⁻
 345 oxidation systems. *Journal of Environmental Management*. 156 (2015) 266-275
- 346 [9] S.K. Ponnaiah, P. Periakaruppan, S. Muthupandian. Ultrasonic energy-assisted in-situ
 347 synthesis of RuO₄/PANI/g-C₃N₄ nanocomposite: Application for picomolar-level
 348 electrochemical detection of endocrine disruptor (Bisphenol-A) in humans and animals.
 349 *Ultrasonics Sonochemistry*. 58 (2019) 104629
- 350 [10] S.Elakkiya, G.Arthanareeswaran, D.B.Das. Embedding low-cost 1D and 2D iron pillared
 351 nanoclay to enhance the stability of polyethersulfone membranes for the removal of
 352 bisphenol A from water. *Separation and Purification Technology*. 266 (2021) 118560
- 353 [11] L.H. Yeh, Z.Y. Huang, Y.C. Liu, M.J. Deng, T.H. Chou, H.C.O. Yang, T. Ahamad, S.M.
 354 Alshehri, K.C.W. Wu. A nanofluidic osmotic power generator demonstrated in polymer
 355 gel electrolytes with substantially enhanced performance. *Journal of Materials Chemistry*
 356 *A*. 7 (2019) 26791-26796.
- 357 [12] L. Joseph, L.K. Boateng, J.R.V. Flora, Y.G. Park, A. Son, M. Badawy, Y. Yoon. Removal
 358 of bisphenol A and 17 α -ethinyl estradiol by combined coagulation and adsorption using
 359 carbon nanomaterials and powdered activated carbon. *Separation and Purification*
 360 *Technology*. 107 (2013) 37-47

- 361 [13] X. Xiao, R. Hao, M. Liang, X.X. Zuo, J.M. Nan, L.S. Li, W.D. Zhang. One-pot
362 solvothermal synthesis of three-dimensional (3D) BiOI/BiOCl composites with enhanced
363 visible-light photocatalytic activities for the degradation of bisphenol-A. *Journal of*
364 *Hazardous Materials*. 233–234 (2012) 122-130
- 365 [14] M.K. Ji, A.N. Kabra, J. Choi, J.H. Hwang, J.R. Kim, R.A.I. Abou-Shanab, Y.K. Oh, B.H.
366 Jeon. Biodegradation of bisphenol A by the freshwater microalgae *Chlamydomonas*
367 *mexicana* and *Chlorella vulgaris*. *Ecological Engineering*. 73 (2014) 260-269.
- 368 [15] G. Sheng, H. Dong, Y. Li. Characterization of diatomite and its application for the
369 retention of radiocobalt: role of environmental parameters. *Journal of Environmental*
370 *Radioactivity*. 113 (2012) 108-115.
- 371 [16] K. Khezri, M. Ghasemi, Y. Fazli. Effect of Mesoporous Diatomite Particles on the
372 Kinetics of SR&NI ATRP of Styrene and Butyl Acrylate. *Zeitschrift für Physikalische*
373 *Chemie*. 232 (2018) 1-17
- 374 [17] W. Tsai, C. Lai, K. Hsien. Characterization and adsorption properties of diatomaceous
375 earth modified by hydrofluoric acid etching. *Journal of Colloid and Interface Science*.
376 297 (2006) 749-754.
- 377 [18] T. Qian, J. Li, H. Ma. Adjustable thermal property of polyethylene glycol/diatomite shape-
378 stabilized composite phase change material. *Polymer Composites*. 37 (2016) 854-860.
- 379 [19] K. Khaldi, M. Hadjel, A. Benyoucef. Removal of Quinmerac by Diatomite and Modified
380 Diatomite from Aqueous Solution. *Surface Engineering and Applied Electrochemistry*.
381 54 (2018) 194-202

- 382 [20] N. Caliskan, A. R. Kul, S. Alkan, E. G. Sogut, I. Alacabey. Adsorption of Zinc(II) on
383 diatomite and manganese-oxide-modified diatomite: A kinetic and equilibrium study.
384 Journal of Hazardous Materials. 193 (2011) 27-36.
- 385 [21] I. Toumi, H. Djelad, F. Chouli, A. Benyoucef. Synthesis of PANI@ZnO Hybrid Material
386 and Evaluations in Adsorption of Congo Red and Methylene Blue Dyes: Structural
387 Characterization and Adsorption Performance. Journal of Inorganic and Organometallic
388 Polymers and Materials. doi.org/10.1007/s10904-021-02084-0
- 389 [22] A. Bekhoukh, I. Moulefera, F.Z. Zeggai, A. Benyoucef, K. Bachari. Anionic Methyl
390 Orange Removal from Aqueous Solutions by Activated Carbon Reinforced Conducting
391 Polyaniline as Adsorbent: Synthesis, Characterization, Adsorption Behavior,
392 Regeneration and Kinetics Study. Journal of Polymers and the Environment.
393 doi.org/10.1007/s10924-021-02248-6
- 394 [23] O. Mahi, K. Khaldi, M. S. Belardja, A. Belmokhtar, A. Benyoucef. Development of a New
395 Hybrid Adsorbent from Opuntia Ficus Indica NaOH Activated with PANI Reinforced
396 and Its Potential Use in Orange G Dye Removal. Journal of Inorganic and
397 Organometallic Polymers and Materials. 31 (2021) 2095-2104.
- 398 [24] M.A. Bekhti, M.S. Belardja, M. Lafjah, F. Chouli, A. Benyoucef. Enhanced tailored of
399 thermal stability, optical and electrochemical properties of PANI matrix containing Al₂O₃
400 hybrid materials synthesized through in situ polymerization. Polymer Composites. 42
401 (2021) 6-14

- 402 [25] E.T. Kang, K.G. Neoh, K.L. Tan. Polyaniline: a polymer with many interesting intrinsic
403 redox states. *Progress in Polymer Science*. 23 (1998) 277-324.
- 404 [26] T. Ahamad, M. Naushad, Y. Alzahrani, S.M. Alshehri. Photocatalytic degradation of
405 bisphenol-A with g-C₃N₄/MoS₂-PANI nanocomposite: Kinetics, main active species,
406 intermediates and pathways. *Journal of Molecular Liquids*. 311 (2020) 113339
- 407 [27] X. Li, X. Li, G. Wang. Surface modification of diatomite using polyaniline. *Materials*
408 *Chemistry and Physics*. 102 (2007) 140-143
- 409 [28] X. Li, X. Li, G. Wang. Fibrillar polyaniline/diatomite composite synthesized by one-step
410 in situ polymerization method. *Applied Surface Science*. 249 (2005) 266-270.
- 411 [29] F. Akti. Photocatalytic degradation of remazol yellow using polyaniline-doped tin oxide
412 hybrid photocatalysts with diatomite support. *Applied Surface Science*. 455 (2018) 931-
413 939
- 414 [30] M.P. Cabrera, T.F. da Fonseca, R.V.B. de Souza, C.R.D. de Assis, J.Q. Marcatoma, J.C.
415 Maciel, D.F.M. Neri, F. Soria, L.B.C. Jr. Polyaniline-coated magnetic diatomite
416 nanoparticles as a matrix for immobilizing enzymes. *Applied Surface Science*. 457
417 (2018) 21-29.
- 418 [31] R. Bhattacharyya, S.K. Ray. Adsorption of industrial dyes by semi-IPN hydrogels of
419 acrylic copolymers and sodium alginate. *Journal of Industrial and Engineering*
420 *Chemistry*. 22 (2015) 92-102.

- 421 [32] B. Wang, G. Zhang, X. Leng, Z. Sun, S. Zheng. Characterization and improved solar light
422 activity of vanadium doped TiO₂/diatomite hybrid catalysts. *Journal of Hazardous*
423 *Materials*. 285 (2015) 212-220.
- 424 [33] F.Z. Kouidri, R. Berenguer, A. Benyoucef, E. Morallon. Tailoring the properties of
425 polyanilines/SiC nanocomposites by engineering monomer and chain substituents.
426 *Journal of Molecular Structure*. 1188 (2019) 121-128
- 427 [34] F. Aouadja, F. Bouzerara, C.M. Guvenc, M.M. Demir. Fabrication and properties of novel
428 porous ceramic membrane supports from the (Sig) diatomite and alumina mixtures.
429 *Boletín de la Sociedad Española de Cerámica y Vidrio*. DOI:
430 10.1016/j.bsecv.2021.04.002.
- 431 [35] J. Mohammed, N.S. Nasri, M.A.A. Zaini, U.D. Hamza, F.N. Ani. Adsorption of benzene
432 and toluene onto KOH activated coconut shell based carbon treated with NH₃.
433 *International Biodeterioration & Biodegradation*. 102 (2015) 245-255.
- 434 [36] H. Nefzi, M. Abderrabba, S. Ayadi, J. Labidi . Formation of Palygorskite Clay from
435 Treated Diatomite and its Application for the Removal of Heavy Metals from Aqueous
436 Solution. *Water*. 10 (2018) 1257.
- 437 [37] S.P. Gupta, H.H. Nishad, S.D. Chakane, S.W. Gosavi, D.J. Late, P.S. Walke. Phase
438 transformation in tungsten oxide nanoplates as a function of post-annealing temperature
439 and its electrochemical influence on energy storage. *Nanoscale Advances*. 2 (2020) 4689-
440 4701.

- 441 [38] G. Sharma, B. Thakur, A. Kumar, S. Sharma, M.Naushad, F.J. Stadler. Atrazine removal
442 using chitin-cl-poly(acrylamide-co-itaconic acid) nanohydrogel: Isotherms and pH
443 responsive nature. *Carbohydrate Polymers*. 241 (2020) 116258.
- 444 [39] M.B. Ahmed, J.L. Zhou, H.H. Ngo, M.A. Johir, K. Sornalingam. Sorptive removal of
445 phenolic endocrine disruptors by functionalized biochar: Competitive interaction
446 mechanism, removal efficacy and application in wastewater. *Chemical Engineering*
447 *Journal*. 335 (2018) 801-811
- 448 [40] J. Wang, M. Zhang. Adsorption Characteristics and Mechanism of Bisphenol A by
449 Magnetic Biochar. *International Journal of Environmental Research and Public Health*.
450 17 (2020) 1075.
- 451 [41] H.Y. Shan. Citation review of Lagergren kinetic rate equation on adsorption reactions.
452 *Scientometrics*. 59 (2004) 171-177.
- 453 [42] S. Lagergren. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, *Kungliga Svenska*
454 *Vetenskapsakademiens. Handlingar*. 24 (1898) 1-39
- 455 [43] S. Azizian. Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and*
456 *Interface Science*. 276 (2004) 47-52
- 457 [44] F. Wang, X. Lu, W. Peng, Y. Deng, T. Zhang, Y. Hu, X.Y. Li. Sorption Behavior of
458 Bisphenol A and Triclosan by Graphene: Comparison with Activated Carbon. *ACS*
459 *Omega*. 2 (2017) 5378-5384.

- 460 [45] I. Langmuir. The adsorption of gases on plane surfaces of glass, mica and platinum.
461 Journal of the American Chemical Society. 40 (1918) 1361-1403
- 462 [46] H.M.F. Freundlich. Over the Adsorption in Solution. Journal of Physical Chemistry. 57
463 (1906) 385-471
- 464 [47] J. Wang, G. Liu, T. Li, C. Zhou. Physicochemical studies toward the removal of Zn(ii) and
465 Pb(ii) ions through adsorption on montmorillonite-supported zero-valent iron
466 nanoparticles. RSC Advances. 5 (2015) 29859.
- 467 [48] M.H. Dehghani, M. Ghadermazi, A. Bhatnagar, P. Sadighara, G.J. Khaniki, B. Heibati, G.
468 McKay. Adsorptive removal of endocrine disrupting bisphenol A from aqueous solution
469 using chitosan. Journal of Environmental Chemical Engineering. 4 (2016) 2647-2655.
- 470 [49] R. Wirasnita, T. Hadibarata, A.R.M. Yusoff, Z. Yusop. Removal of bisphenol A from
471 aqueous solution by activated carbon derived from oil palm empty fruit bunch. Water,
472 Air, & Soil Pollution. 225 (2014) 2148.
- 473 [50] A. Nakanishi, M. Tamai, N. Kawasaki, T. Nakamura, S. Tanada. Adsorption
474 characteristics of bisphenol A onto carbonaceous materials produced from wood chips as
475 organic waste. Journal of Colloid and Interface Science. 252 (2002) 393–396.
- 476 [51] Y. Zhou, L. Chen, P. Lu, X. Tang, J. Lu. Removal of bisphenol A from aqueous solution
477 using modified fibric peat as a novel biosorbent. Separation and Purification Technology
478 81 (2011) 184–190.

- [52] X. Men, Q. Guo, B. Meng, S. Ren, B. Shen. Adsorption of bisphenol A in aqueous solution by composite bentonite with organic moiety. Microporous and Mesoporous Materials. 308 (2020) 110450.
- [53] Q. Zhou, Y. Wang, J. Xiao, H. Fan.. Adsorption and removal of bisphenol A, α -naphthol and β -naphthol from aqueous solution by Fe_3O_4 @polyaniline core-shell nanomaterials. Synthetic Metals. 212 (2016) 113-122.
- [54] Q. Zhou, Y. Wang, J. Xiao, H. Fan.. Fabrication and characterisation of magnetic graphene oxide incorporated Fe_3O_4 @polyaniline for the removal of bisphenol A, t-octylphenol, and α -naphthol from water. Scientific Reports. 7 (2017) 11316.
- [55] M. Zeeshan, J. Shah, M.R. Jan, M. Iqbal. Removal of Bisphenol-A from Aqueous Samples Using Graphene Oxide Assimilated Magnetic Silica Polyaniline Composite. Journal of Inorganic and Organometallic Polymers and Materials. 31 (2021) 2073–2082
- [56] D. Bhatia, D. Datta. Removal of Bisphenol-A Using Amine-Modified Magnetic Multiwalled Carbon Nanotubes: Batch and Column Studies. Journal of Chemical & Engineering Data. 64 (2019) 2877-2887

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 mg.L⁻¹; pH: 6.0; T: 298K; adsorbent dose: 1g), (c) Adsorption isotherms (adsorbent dose: 1g; BPA 25 mL; T: 298 K; pH: 6.0) and (d) Adsorbent capacity change and first BPA in consecutive cycles (adsorbents dose: 1g; BPA: 25mL; T: 298K; pH 6.0).

516 **Table 1.** XPS values of Binding Energy (BE) for: (A) PANI, (B) KG and (C) PANI@KG
517 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

518

519 **Table 2.** Textural properties of materials.

Materials	<i>BET area</i> (<i>S_{BET}</i>) m ² .g ^{–1}	<i>Total pores volume</i> (<i>V_t</i>) cm ³ .g ^{–1}	<i>Mesoporous volume</i> (<i>V_{mes}</i>) 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

520

521 **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

522

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_o 500 mg.L⁻¹.

Materials	$Q_{eq.Exp}$ (mg.g ⁻¹)	PFO			PSO		
		k_I min ⁻¹	$Q_{eq.Cal}$ mg.g ⁻¹	R^2	$k_{2,ads}$ g.mg ⁻¹ .min ⁻¹	$Q_{eq.Cal}$ 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 (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R_L	R^2	K_F (mg ^{1-1/n} L ^{1/n} 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

536 **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

537

Figures

Figure 1

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

Figure 2

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