

Removal of ciprofloxacin from aqueous solution by activated carbon prepared from orange peel using zinc chloride

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Abstract. In this study, the removal of Ciprofloxacin (CPX) from aqueous solutions was investigated by a new activated carbon adsorbent prepared from orange peel (ACOP) with chemical activation using ZnCl_2 . The physicochemical properties of orange peel activated carbon were characterized by proximate and ultimate analysis, scanning electron microscopy, BET surface area determination and Fourier transformation infrared spectroscopic studies. According to Brunauer–Emmett–Teller isotherm and non-local-density functional theory, the cumulative surface area, pore volume and pore size of ACOP were determined as $1193 \text{ m}^2 \text{ g}^{-1}$, 0.83 cc g^{-1} and 12.7 Å , respectively. The effects of contact time, pH, temperature and ACOP dose on the batch adsorption of CPX were studied. Adsorption equilibrium data of CPX with ACOP were found to be compatible with both the Langmuir and Freundlich isotherms. CPX adsorption capacity of ACOP was calculated as 181.8 mg g^{-1} using Langmuir isotherm. The CPX adsorption kinetics were found to be harmonious with the pseudo-second-order kinetic model. Conclusively, ACOP can be assessable as an effective adsorbent for the removal of ciprofloxacin (CPX) from aqueous solutions.

Keywords: activated carbon; aqueous solution; ciprofloxacin; orange peel; removal

1. Introduction

Antibiotics used for treating of many diseases are frequently encountered in domestic and hospital wastewater. Antibiotics accumulating in water bodies through anthropogenic sources also affect ecological health (Agboola and Bello 2020). Ciprofloxacin (CPX) is one of the chemotherapeutic antibiotics among the fluoroquinolones widely used around the world (Githinji *et al.* 2011, Igwegbe *et al.* 2021). While the CPX concentration is $<1 \text{ µg L}^{-1}$ in water and wastewater (Carmosini and Lee 2009), this value exceeds 150 µg L^{-1} in hospital wastewater (El-Shafey *et al.* 2012). The presence of CPX in aquatic environments can bring about the growth of antibiotic-resistant bacteria that are harmful to human health (Wang *et al.* 2015). For this reason, studies on the removal of CPX and similar antibiotics from wastewater have increased recently. Considering that conventional wastewater treatment processes do not provide effective removal for CPX, researches on various advanced methods and techniques such as oxidation (Mondal *et al.* 2018, Ganesan *et al.* 2019), membrane separation (Palacio *et al.* 2018, Bhattacharya *et al.* 2019) and adsorption (Darweesh and Ahmed 2017, Duan *et al.* 2018, Mohammed *et al.* 2019, Antonelli *et al.* 2020, Al-Musawi *et al.* 2021) have been emphasized in the literature. Adsorption is preferred for the removal of drugs and heavy metals from aqueous solutions as an easy-to-

apply method and inexpensive activated carbons (AC) production (Ozer and Imamoglu 2017, Usanmaz *et al.* 2021). Various AC fabricated from agricultural wastes such as bamboo (Wang *et al.* 2015), rice husk (Zhang *et al.* 2017), oat hulls (Movasaghi *et al.* 2019), corn cob and rice husk (Peñafiel *et al.* 2019), pomegranate peels (Mekhamer and Al-Tamimi 2019), prosopis juliflora (Chandrasekaran *et al.* 2020), banana stalk (Agboola and Bello 2020) and sugarcane bagasse (Peñafiel *et al.* 2021) have been used for CPX removal.

Orange peels have also been used for the preparation of AC using various activating agents such as potassium carbonate (Foo and Hameed 2012), phosphoric acid (Fernandez *et al.* 2014), and sulfuric acid, sodium hydroxide, potassium hydroxide, zinc chloride (ZnCl_2) and phosphoric acid (Bediako *et al.* 2020) and these AC's were used for the removal of methylene blue from aqueous solutions. Removal of malachite green (Lam *et al.* 2017) and azo dye (Munagapati and Kim, 2016) was carried out using AC from orange peel prepared by activation using sodium hydroxide. In another study, Cr(VI) removal with activated carbon from orange peel synthesized with chemical activation using ZnCl_2 was also studied (El Nemr *et al.* 2020). But no study was found in our literature survey for use of an orange peel activated carbon (ACOP) prepared with ZnCl_2 activation for the removal of CPX from aqueous solutions.

Orange peel is real waste which product of fruit juice industries. This waste occurs in large quantities at Mediterranean region from the factories. Hence, conversion of orange peel to activated carbon eliminates to disposal of solid waste problems and valorizes the fruit waste by

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producing activated carbon. While heavy metal adsorption with activated carbons has been widely investigated by researchers, removal of drugs has not been studied in detail. So, many studies about removal of pharmaceuticals from aqueous solutions have been increased in the last decade. Hence, investigation of CPX removal using orange peel activated carbon is very important.

In this study, activated carbon was prepared from orange peel with chemical activation using ZnCl_2 and used for batch removal of CPX from aqueous solutions. The surface and pore characterization, and physicochemical properties of the adsorbent were studied. To determine the effects of contact time, ACOP dose, pH and temperature on the CPX removal, batch adsorption experiments were performed. Equilibrium and kinetics of CPX adsorption onto ACOP were also examined using isotherms and kinetic models.

2. Materials and methods

2.1 Instruments and chemicals

The temperature-controlled orbital shaker (KS4000i, IKA®-Werke GmbH and Co. KG, Staufen, Germany) was used for shaking Erlenmeyer containing a suspension of ACOP and CPX in the batch adsorption experiments. CPX concentration was analyzed using UV-Spectrophotometer (Shimadzu UV 2600, Shimadzu Corporation, Kyoto, Japan). ACOP was fabricated in the tube furnace (Protherm PTF 12, Alser Teknik Seramik A.Ş., Ankara, Turkey) under nitrogen atmosphere. Infrared spectra were determined using a Perkin Elmer Spectrum Two FTIR spectrophotometer at 4 cm^{-1} resolution in ATR mode using a ceramic light source (Perkin Elmer®, Shelton, CT, USA). Surface morphology of the ACOP was carried out using scanning electron microscopy (SEM) (FEI, Quanta FEG 250, USA) at Düzce University Scientific and Technological Research Application and Research Center, Düzce, Turkey. Brunauer–Emmett–Teller (BET) surface area determination, non-local-density functional theory (NLDFT) pore structure analysis was carried out using Quantachrome Autosorb-6B (Quantachrome Ins., FL, USA) and CHN elemental analysis was performed using the Leco CHNS 932 analyzer (LECO Corporation, MI, USA) at METU Central Laboratory, Ankara, Turkey. CPX stock solution was prepared from C17H18FN3O3HCl.H2O (supplied by Deva Holding A.Ş., Istanbul, Turkey) at 250 mg L^{-1} , standard and working solutions were prepared by daily dilution of the stock solution. The pH measurement of the CPX solutions was performed using Schott CG 840 pH meter (Schott AG, Mainz, Germany). The pH of the working solutions was adjusted using HCl (0.1 M) and NaOH (0.1 M) solutions by controlling with the pH meter.

2.2 Preparation and characterization of ACOP

Oranges purchased from Sakarya's local markets were peeled. The peels were washed with deionized water and dried at 105°C for 48 h. Equal amounts (90 g) of ZnCl_2 and orange peel, and distilled water (150 mL) were mixed and then, maintained at room temperature for 24 hours for the

impregnation of ZnCl_2 . Then, it was dried at 105°C for 24 h. The impregnated material was pyrolyzed for 1 h under N_2 flow (100 mL min^{-1}) in a tube furnace at 700°C . After its cooling down to ambient temperature under N_2 flow, the pyrolyzed material was obtained. The material was added to 100 mL of 2 M HCl solutions for 5 h at 70°C . The material was washed with deionized water until no chloride ions were observed in the effluents checked by 0.1 M AgNO_3 . The obtained orange peel activated carbon was dried at 105°C and then stored in brown glass bottle and used in further studies.

The ACOP was characterized with FTIR technique, SEM images, BET and NLDFT (Neimark 1995, Ravikovitch *et al.* 1995) methods. To define the functional groups on the surface of ACOP the FTIR spectra were recorded between 4000 and 400 cm^{-1} . The adsorption mechanism and porous structure of ACOP were evaluated with a nitrogen adsorption-desorption curve using BET and NLDFT methods. CHN elemental analyses were performed to determine the content of ACOP. Iodine number (ASTM D4607-94 1999), moisture (ASTM D2867-99 1999), ash (ASTM D2866-94 2004) and volatile matter (ASTM D5832-95 1998) were also determined.

2.3 Adsorption studies

Batch adsorption studies were carried out to investigate ACOP efficiency for removal of CPX from aqueous solutions under variable conditions such as pH (3-9), initial CPX concentration ($25\text{--}500\text{ mg L}^{-1}$), contact time (5-1440 min), ACOP dose (25-300 mg). The temperature effect was studied at 25, 35 and 45°C . Experimental studies were conducted (except for pH effect) at the original pH of the CPX solution, stirring speed of 180 rpm, 24 h contact time and 25°C . The remaining CPX level in the solutions after adsorption was measured using a UV spectrophotometer at a wavelength of 276 nm. The amount of CPX adsorbed per gram of ACOP (q_e) and adsorption percentage (%) were calculated using the following Eqs. (1) and (2), respectively;

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

$$\text{Adsorption, \%} = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (2)$$

where C_0 and C_e are initial and equilibrium CPX concentrations (mg L^{-1}), respectively, V is the CPX solution volume (L), and m is ACOP amount (g) (Kiraz *et al.* 2019).

3. Results and discussion

3.1 Characterization of ACOP

The C,H,N content, moisture, ash and volatile matter and other characteristic properties of ACOP are listed in Table 1. The pore structure and carbon content of the adsorbent are important factors affecting the adsorption efficiency. According to elemental analysis results, ACOP has high carbon (77.2%), and low hydrogen (2.1%) and

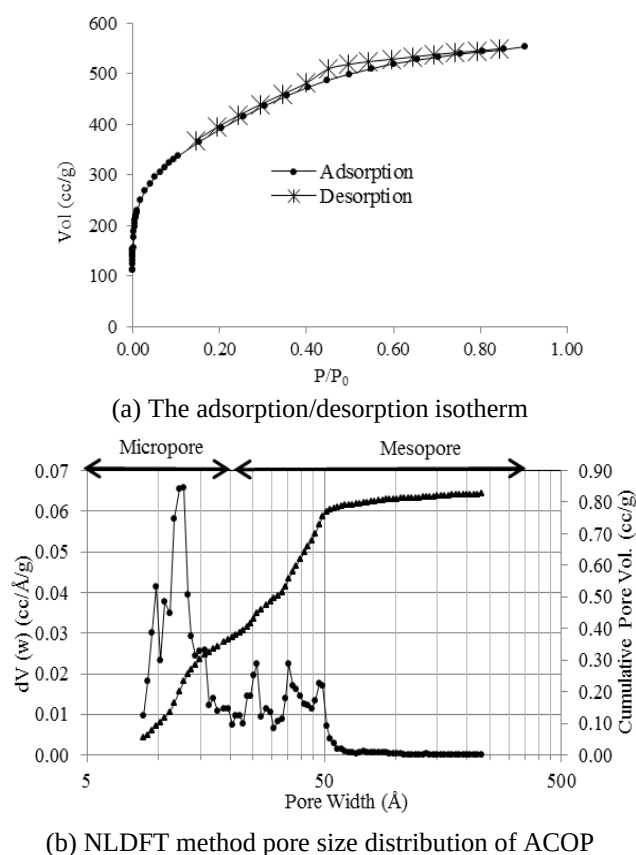


Fig. 1 BET analysis results

Table 1 Characteristics of ACOP

Elemental analysis (%)	
C	77.2
H	2.1
N	2.8
Proximate analyses (%)	
Moisture	9.6
Ashes	0.2
Volatile matter	23.7
Fixed carbon	76.1
Iodine number (mg g ⁻¹)	705.7
pH _{pzc}	4.2
BET surface area (m ² g ⁻¹)	1384
NLDFT Cum. surface area (m ² g ⁻¹)	1193
Total pore volume (cc g ⁻¹)	0.83
Micropore volume (cc g ⁻¹)	0.59
Pore size (Å)	12.7

nitrogen (2.8%) contents. Moisture, ash and volatile matter properties of ACOP were found to be 9.6%, 0.2% and 23.7%, respectively, resulting in high fixed carbon (76.1%) content. With this high fixed carbon content and low ash content, ACOP can be accepted as an effective activated carbon (Zhang *et al.* 2020).

According to the IUPAC classifications of physical adsorption isotherms and related hysteresis loops, the N₂

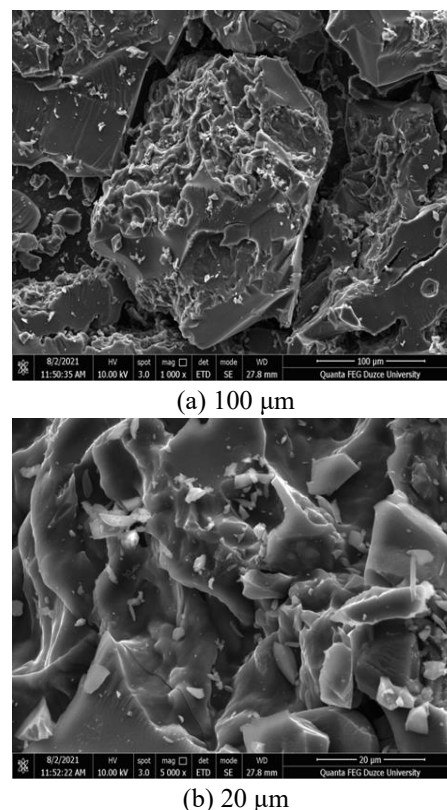


Fig. 2 SEM images of ACOP

adsorption isotherm obtained with ACOP shown in Fig. 1a is compatible with type I isotherm and H4 hysteresis loops. Type I isotherm is observed in carbon with pore size distributions in a wide range consisting of wide micropores and narrow mesopores, and H4 loops are observed in micro-meso type porous carbons (Thommes *et al.* 2015). The ACOP isotherm conforms to the type I isotherm, where micropore filling occurs at low P/P_0 (Sun *et al.* 2016).

The multi-point BET surface area of the ACOP was determined as 1384 m² g⁻¹ and the NLDFT Method provided a cumulative surface area as 1193 m² g⁻¹. ACOP has a total pore volume of 0.83 cc g⁻¹ and a micropore volume of 0.59 cc g⁻¹. Based on Fig. 1(b) and the pore volume data, a high percentage of micro type pores and a lower percentage of meso type pores were defined for ACOP. According to the pore size distribution curve (Fig 1(b)), it was determined that the pore size ranged between 8 and 250 Å and the average pore size of ACOP was 12.7 Å. This value shows that the structure of the ACOP is mainly composed of micropores and the ACOP can be preferred in industrial applications (Ahmed and Theydan 2014). According to literature, chemically activated microporous ACs can efficiently remove small molecules such as drug active ingredients (Mansour *et al.* 2018). The iodine number of ACOP was obtained as 705.7 mg g⁻¹. This result is also compatible with the literature, for example, Aygün *et al.* (2003) calculated the iodine numbers of almond shell and apricot stone activated carbons as 638 and 754 mg g⁻¹, respectively.

The morphological structure of ACOP was evaluated with the SEM images shown in Fig. 2. The ACOP surface

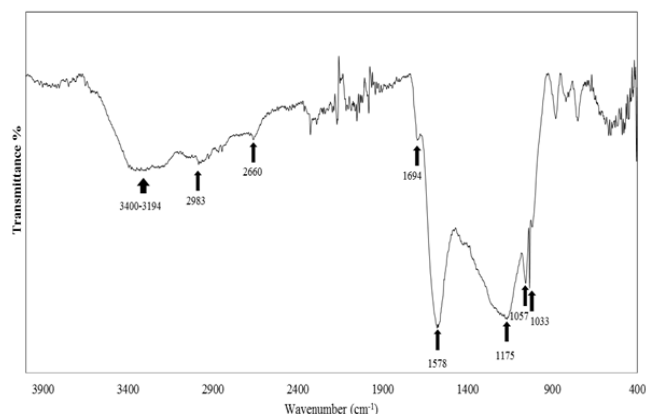
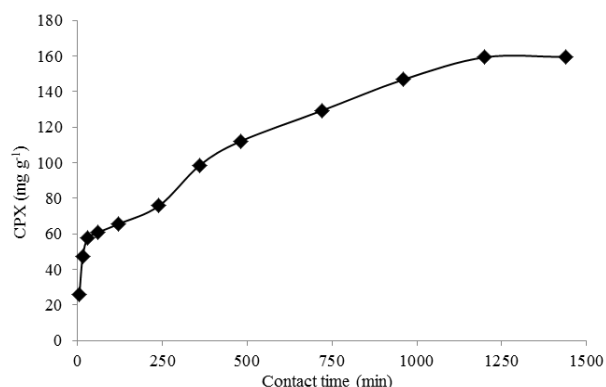
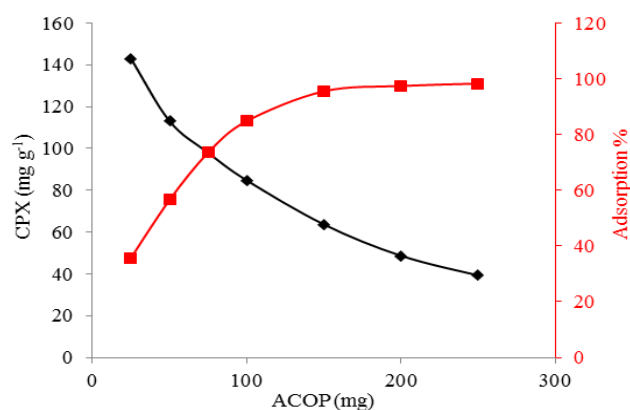


Fig. 3 FT-IR spectra of ACOP

Fig. 4 Effect of contact time on the removal of ciprofloxacin by orange peel activated carbon (C_0 :400 mg L⁻¹, V: 50 mL, m:50 mg, pH:6, T:25 °C)Fig. 5 Effect of orange peel activated carbon dosage on the removal of ciprofloxacin (C_0 :200 mg L⁻¹, V: 50mL, m:50 mg, pH:6, T:25 °C)

was determined as a heterogeneous consisting of grooves, passages, and pores of various sizes. ACOP has a large surface area for adsorbate removal, as confirmed by its BET surface area determination results (Mohammed *et al.* 2019).

To characterize the surface functional groups of ACOP, the FTIR spectrum of ACOP is shown in Fig. 3. In the spectrum, O–H stretching vibration occurs was observed at wavenumbers ranged between 3400 and 3194 cm⁻¹ (Pua *et al.* 2013). The peaks at 2983 cm⁻¹ and 2660 cm⁻¹ regions represent C–H stretching (Chen *et al.* 2012). There is an

C=O stretching at 1694 cm⁻¹ (Dutta 2017). A wavenumber of 1578 cm⁻¹ may be attributed to stretching of the C=C groups (Imamoglu *et al.* 2018). The peaks between 1175 and 1033 cm⁻¹ can be ascribed to stretching of the C–O groups of alcoholic, etheric and acidic structures (Imamoglu *et al.* 2016).

3.2 Effect of contact time

The effect of contact time on the CPX adsorption was determined by performing studies at an initial concentration of 400 mg L⁻¹ CPX at contact times between 5 and 1440 min. According to the results shown in Fig. 4, CPX adsorption increased very rapidly in the first 60 min. and slowly increased between 120 min. and 1200 min., and then reached equilibrium conditions at 1200 min. The adsorption capacity of ACOP at equilibrium time was determined as 159.3 mg g⁻¹. The adsorption sites on the ACOP surface were initially null and accessible. However, once equilibrium is reached, the ACOP surface becomes saturated and adsorption sites of ACOP for CPX are depleted (Ozer 2020). The equilibrium time for adsorption of CPX onto AC from lignin by H₃PO₄ was found to be 1000 min (Huang *et al.* 2014). CPX adsorption onto bamboo based activated carbon was reached to equilibrium at 4320 min (Wang *et al.* 2015).

3.3 Effect of ACOP dosage

The percentage removal of CPX and adsorbed amount of CPX per gram of ACOP depending on the ACOP dosages are shown in Fig. 5 using ACOP amounts between 0.025 and 0.25 g for 50 mL of CPX solutions at 200 mg L⁻¹. The percentage of CPX removal increases with increasing ACOP amount because higher adsorbent dose creates higher adsorption sites for fixed number of CPX molecules (Li *et al.* 2017, Bal *et al.* 2021).

However, due to the inverse ratio between ACOP amount and q_e , the amount of CPX adsorbed per gram of ACOP decreased with increasing ACOP dose. Zhang *et al.* (2017) showed that CPX adsorption decreased with increasing amount of activated carbon derived from the residue of desilicated rice husk. As can be seen from the adsorption percentage curve from the Fig. 5, the optimum ACOP dose was determined as 150 mg.

3.4 Effect of temperature

The effect of temperature on the removal of CPX was investigated by adding 50 mg ACOP to CPX solution (100 mg L⁻¹) at different temperatures (25, 35, 45°C). As seen in Fig. 6, the CPX adsorption onto ACOP increased with an increase in temperature. Hence, it was concluded that the adsorption of CPX onto ACOP is endothermic (Peng *et al.* 2018). Similarly, Zhang *et al.* (2011) and Ahmed and Theydan (2014) reported that CPX removal increased with an increase in temperature.

3.5 Effect of pH

pH is an important factor in the adsorption of pharmaceuticals due to the surface charge of the adsorbent and ionization of the drug molecules (Peñafiel *et al.* 2019).

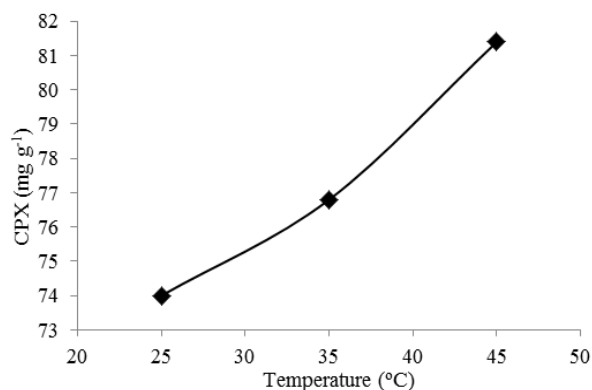


Fig. 6 Effect of temperature on the removal of ciprofloxacin from aqueous solutions (C0:100 mg L⁻¹, V: 50 mL, m: 50 mg, pH:6)

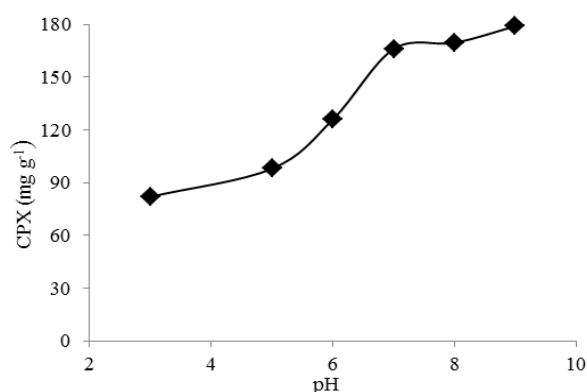


Fig. 7 Effect of pH on the removal of ciprofloxacin from aqueous solutions by orange peel activated carbon (C0:50 mg L⁻¹, V: 50mL, m: 10 mg, T:25 °C)

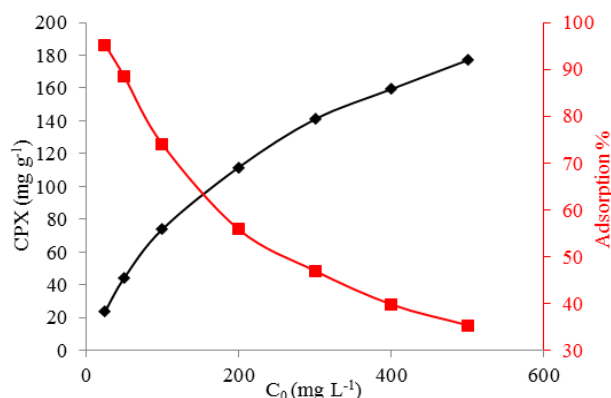


Fig. 8 Effect of initial concentration of ciprofloxacin on its removal from aqueous solutions (V: 50mL, m:50 mg, pH:6, T:25 °C)

The effect of pH on CPX removal by ACOP was studied at pH between 3 and 9.

The CPX molecule is a neutral molecule containing both positive and negative charges. CPX exhibits cationic properties at pH ≤ 4.0, anionic at pH > 8, and cationic and zwitterionic properties between pH 4.0 and 8.0 (Duan *et al.* 2018). The pH_{pzc} value of the ACOP was determined as 4.2. As seen in Fig. 7, low adsorption capacity was observed in the case of pH < 4.2, which resulted from less electrostatic

Table 2 Langmuir, Freundlich isotherms and correlation coefficients for ciprofloxacin adsorption onto ACOP

Isotherm	Equation	Constants	Values	Reference
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}}$	q_{max} (mg g ⁻¹)	181.8	(Langmuir 1918)
		$K_L \times 10^2$ (L mg ⁻¹)	3.30	
		r^2	0.98	
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	K_F	22.97	(Freundlich 1906)
		n	2.81	
		r^2	0.99	

attraction between CPX and the ACOP surfaces, and competition between CPX and H⁺ ions (Wang *et al.* 2017). At pH between 6 and 8, an electrostatic interaction occurs between the positively charged CPX and the negatively charged ACOP surface (El-Shafey *et al.* 2012). In this study, the maximum adsorption capacity was obtained as 170 mg g⁻¹ at a pH of 8.0. But for practical reasons, the adsorption of CPX by ACOP in the next studies was carried out at the original pH of the CPX solution at pH of 6.0. CPX adsorption using activated carbon prepared from *Enteromorpha prolifera* (Wang *et al.* 2015) and surface-modified carbon materials (Carabineiro *et al.* 2011) was performed at the original pH value of CPX.

3.6 Effect of initial concentration

To determine the effect of CPX initial concentrations on adsorption, initial concentrations of CPX between 25 and 500 mg L⁻¹ were used. The obtained results are shown in Fig. 8.

The percentage of CPX adsorption varied between 95.2 and 35.4%. The CPX adsorption increased from 23.8 mg g⁻¹ to 177.05 mg g⁻¹ by increasing the CPX initial concentration from 25 to 500 mg L⁻¹. This is due to the limited number of adsorption zone on the ACOP surface to uptake all CPX molecules at high concentration of CPX (Al-Musawi *et al.* 2021). Mao *et al.* (2016) reports that as the initial concentration increases from 10 to 60 mg L⁻¹, the removal of CPX decreases from 98% to 59.9%.

3.7 Ciprofloxacin adsorption isotherms by ACOP

The equation of the models and the calculated values for the CPX adsorption onto ACOP are shown in Table 2.

The equilibrium data of CPX adsorption onto ACOP were analysed using the Langmuir and Freundlich isotherm models at 25°C. Linear graphics of the isotherm models for the CPX adsorption onto ACOP are shown in Fig. 9. Langmuir and Freundlich isotherm models produced correlation coefficients to be close to each other at $r^2 = 0.98$ and $r^2 = 0.99$, respectively. Hence, it was concluded that the adsorption of CPX onto ACOP was followed by both the Langmuir and Freundlich isotherms. Langmuir isotherm explains that the adsorption process is a monolayer and limited adsorption (Kalhori *et al.* 2017). Fitting the Freundlich isotherm model is an indicator of multilayer physical adsorption (Hameed *et al.* 2007).

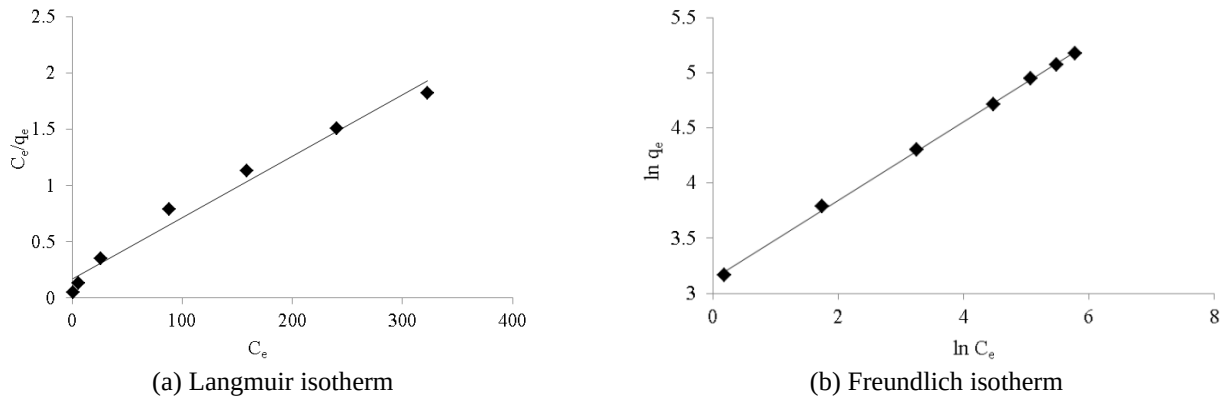


Fig. 9 Linear isotherm graphs for ciprofloxacin adsorption onto orange peel activated carbon

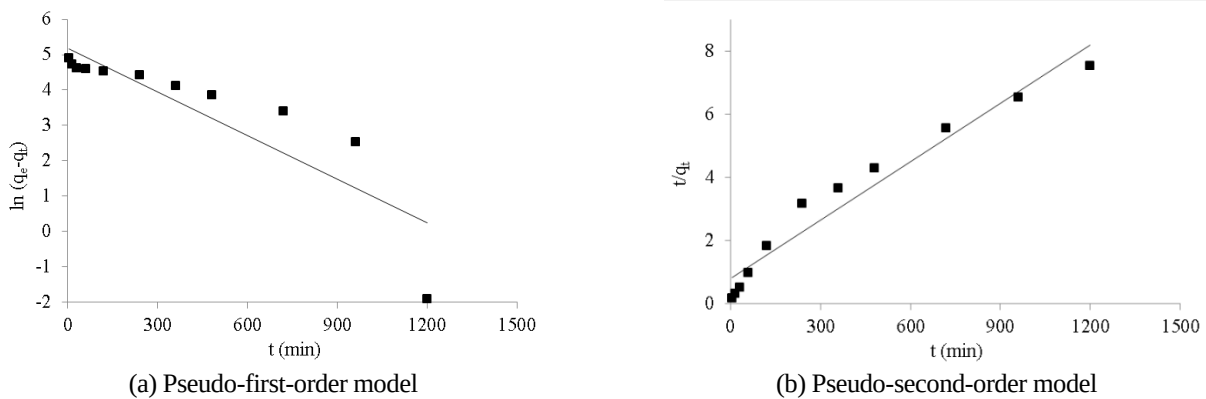


Fig. 10 Kinetic charts for ciprofloxacin adsorption onto orange peel activated carbon

Table 3 Comparison of the recent CPX adsorption studies

Adsorbent	Activation	pH	Contact time (min)	Best-fit Kinetic	Best fit Isotherm	Qmax (mg g ⁻¹)	Reference
Coal Fly Ash	Sodium hydroxide	-	100	Pseudo 2 nd order	Langmuir	1.5	(Zhang <i>et al.</i> 2011)
Palm Leaflet	Sulphuric acid	6	2880	Pseudo 2 nd order	Langmuir	133.3	(El-Shafey <i>et al.</i> 2012)
Coal Fly Ash	No activation	4	270	Pseudo 2 nd order	Freundlich	17.5	(Maheshwari <i>et al.</i> 2013)
Lignin	Phosphoric acid	5.5	1000	Pseudo 2 nd order	Langmuir	418.6	(Huang <i>et al.</i> 2014)
Enteromorpha Prolifera	Pyrophosphoric Acid	6-9	360	Pseudo 2 nd order	Langmuir	216.5	(Gao <i>et al.</i> 2015)
Bamboo	Phosphoric acid	5.10	4320	Pseudo 2 nd order	Langmuir	613	(Wang <i>et al.</i> 2015)
Rice Husk	Physical activation	7.9	307	Pseudo 2 nd order	Langmuir	461.9	(Zhang <i>et al.</i> 2017)
Oat Hulls	Phosphoric acid	7	-	Pseudo 2 nd order	Freundlich	83	(Movasaghi <i>et al.</i> 2019)
Pomegranate Peels	No activation	4-5	120	Pseudo 2 nd order	Langmuir	999	(Mekhamer and Al-Tamimi 2019)
Corn Cob	No activation	6	40	Pseudo 2 nd order	Freundlich	26.3	(Peñafiel <i>et al.</i> 2019)
Banana Stalk	Orthophosphoric acid	8	420	Pseudo 2 nd order	Langmuir	49.8	(Agboola and Bello 2020)
Sugarcane Bagasse	No activation	6-8	60	Pseudo 2 nd order	Freundlich	5.7	(Peñafiel <i>et al.</i> 2021)
Orange Peel	Zinc chloride	6	1200	Pseudo 2 nd order	Langmuir	181.8	This work

Also, the n value obtained from Freundlich isotherm is greater than 1 showing the suitability of the adsorption to Freundlich model (Yin *et al.* 2018).

The separation factor R_L value of the Langmuir isotherm model for the adsorption of CPX onto ACOP was calculated using Eq. (3) given below.

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where K_L (L mg⁻¹) is a constant of Langmuir, R_L is a separation factor and C_0 is the initial concentration (mg L⁻¹) (Eze *et al.* 2021, Öztürk *et al.* 2021). R_L value for the

Table 4 Kinetics and correlation coefficients for ciprofloxacin adsorption onto ACOP

Kinetic model	Equation	Constants	Values	Ref.
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	k_1	4.1×10^{-3}	(Lagergren 1898)
		q_e (mg g ⁻¹)	179.8	
		r^2	0.77	
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{t}{q_e}$	k_2	4.8×10^{-5}	(Ho and McKay 1999)
		q_e (mg g ⁻¹)	161.3	
		r^2	0.95	

adsorption of CPX was found to be 0.07 indicating spontaneity of the adsorption (Sayın *et al.* 2017).

For comparison of ACOP adsorption capacity with other adsorbents, the CPX adsorption capacities of various activated carbons from different natural materials with different activation methods are shown in Table 3. The CPX capacities are ranged between 1.5 mg g⁻¹ by coal fly ash (Zhang *et al.* 2011) and 999 mg g⁻¹ by pomegranate peels (Mekhamer and Al-Tamimi, 2019). It can be concluded that ACOP has moderate CPX adsorption capacity.

3.7 Ciprofloxacin adsorption kinetics by ACOP

The CPX adsorption kinetics by ACOP were determined using pseudo-first-order and pseudo-second-order kinetic models and their linear curves illustrated in Fig 10. The equation of the models and their calculated coefficients are given in Table 4.

The predicted q_e value by the pseudo-second order model was found to be quite close to the experimental ones. The correlation coefficients of the pseudo-second order model was calculated as 0.95. The proximity of the q_e value estimated by the kinetic models and the experimentally found q_e value is also important to conclude which model fits the CPX adsorption kinetics (Carabineiro *et al.* 2011). In this study, the q_e value (161.3 mg g⁻¹) estimated by the pseudo-second order kinetic model is closer to the experimental q_e value (159.3 mg g⁻¹) found for the adsorption of CPX onto ACOP. Hence, it was concluded that the CPX adsorption kinetics by ACOP were in accordance with the pseudo-second-order kinetic model.

4. Conclusions

In this study, a newly produced activated carbon from orange peel for removal of CPX, an antibiotic, which is an important pollution problem in wastewater, was investigated. Activated carbon obtained from the orange peel with the activation of ZnCl₂ was used for CPX removal with its large surface area and micropore structure. The average pore size of ACOP was found to be 12.73 Å. In the batch adsorption experiments of CPX, it was determined that variables such as contact time, pH and temperature affect the removal of CPX. The adsorption of CPX was favored at pH of 8.0 and reached equilibrium at 1200 min. The increasing of temperature caused an increase in the CPX adsorption. The adsorption of CPX with ACOP was

determined to be endothermic process. CPX adsorption equilibrium data by ACOP were found to be compatible with both Langmuir and Freundlich isotherms. The maximum CPX adsorption capacity of ACOP was found to be 181.8 mg g⁻¹ from the Langmuir equation. The CPX adsorption followed the pseudo-second-order kinetic models. It was concluded that ACOP can be used as an effective adsorbent for the removal of CPX from wastewater.

References

- Agboola, O.S. and Bello, O.S. (2020), "Enhanced adsorption of ciprofloxacin from aqueous solutions using functionalized banana stalk", *Biomass Convers. Biorefinery.*, 1-16. <https://doi.org/10.1007/s13399-020-01038-9>.
- Ahmed, M.J. and Theydan, S.K. (2014), "Fluoroquinolones antibiotics adsorption onto microporous activated carbon from lignocellulosic biomass by microwave pyrolysis", *J. Taiwan Inst. Chem. Eng.*, **45**(1), 219-226. <https://doi.org/10.1016/j.jtice.2013.05.014>.
- Al-Musawi, T.J., Mahvi, A.H., Khatibi, A.D. and Balarak, D. (2021), "Effective adsorption of ciprofloxacin antibiotic using powdered activated carbon magnetized by iron(III) oxide magnetic nanoparticles", *J. Porous Mater.*, **28**(3), 835-852. <https://doi.org/10.1007/s10934-021-01039-7>.
- Antonelli, R., Malpass, G.R.P., Da Silva, M.G.C. and Vieira, M.G.A. (2020), "Adsorption of ciprofloxacin onto thermally modified bentonite clay: Experimental design, characterization, and adsorbent regeneration", *J. Environ. Chem. Eng.*, **8**(6), 104553. <https://doi.org/10.1016/j.jece.2020.104553>.
- ASTM D5832-98 (1998), *Standard test method for volatile matter content of activated carbon samples*, ASTM International, West Conshohocken, Pennsylvania, U.S.A.
- ASTM D4607-94 (1999), *Standard test method for determination of iodine number of activated carbon*, ASTM International, West Conshohocken, Pennsylvania, U.S.A.
- ASTM D2867-99 (1999), *Standard test methods for moisture in activated carbon*, ASTM International, West Conshohocken, Pennsylvania, U.S.A.
- ASTM D2866-94 (2004), *Standard test method for total ash content of activated carbon*, ASTM International, West Conshohocken, Pennsylvania, U.S.A.
- Bal, D., Özer, Ç. and İmamoğlu, M. (2021), "Green and ecofriendly biochar preparation from pumpkin peel and its usage as an adsorbent for methylene blue removal from aqueous solutions", *Water Air Soil Pollut.*, **232**(11). <https://doi.org/10.1007/s11270-021-05411-w>.
- Bediako, J.K., Lin, S., Sarkar, A.K., Zhao, Y., Choi, J.W., Song, M.H., Cho, C.W. and Yun, Y.S. (2020), "Evaluation of orange peel-derived activated carbons for treatment of dye-

- contaminated wastewater tailings", *Environ. Sci. Pollut. Res.*, **27**(1), 1053-1068. <https://doi.org/10.1007/s11356-019-07031-8>.
- Bhattacharya, P., Mukherjee, D., Dey, S., Ghosh, S. and Banerjee, S. (2019), "Development and performance evaluation of a novel CuO/TiO₂ ceramic ultrafiltration membrane for ciprofloxacin removal", *Mater. Chem. Phys.*, **229**, 106-116. <https://doi.org/10.1016/j.matchemphys.2019.02.094>.
- Carabineiro, S.A.C., Thavorn-Amornsri, T., Pereira, M.F.R. and Figueiredo, J.L. (2011), "Adsorption of ciprofloxacin on surface-modified carbon materials", *Water Res.*, **45**(15), 4583-4591. <https://doi.org/10.1016/j.watres.2011.06.008>.
- Carmosini, N. and Lee, L. S. (2009), "Ciprofloxacin sorption by dissolved organic carbon from reference and bio-waste materials", *Chemosphere*, **77**(6), 813-820. <https://doi.org/10.1016/j.chemosphere.2009.08.003>.
- Chandrasekaran, A., Patra, C., Narayanasamy, S. and Subbiah, S. (2020), "Adsorptive removal of Ciprofloxacin and Amoxicillin from single and binary aqueous systems using acid-activated carbon from *Prosopis juliflora*", *Environ. Res.*, **188**, 109825. <https://doi.org/10.1016/j.envres.2020.109825>.
- Chen, Y., Mastalerz, M. and Schimmelmann, A. (2012), "Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy", *Int. J. Coal Geol.*, **104**, 22-33. <https://doi.org/10.1016/j.coal.2012.09.001>.
- Darweesh, T.M. and Ahmed, M.J. (2017), "Adsorption of ciprofloxacin and norfloxacin from aqueous solution onto granular activated carbon in fixed bed column", *Ecotox. Environ. Safe.*, **138**, 139-145. <https://doi.org/10.1016/j.ecoenv.2016.12.032>.
- Duan, W., Wang, N., Xiao, W., Zhao, Y. and Zheng, Y. (2018), "Ciprofloxacin adsorption onto different micro-structured tourmaline, halloysite and biotite", *J. Mol. Liq.*, **269**, 874-881. <https://doi.org/10.1016/j.molliq.2018.08.051>.
- Dutta, A. (2017), *Fourier Transform Infrared Spectroscopy In Spectroscopic Methods for Nanomaterials Characterization*, Elsevier Inc.
- El-Shafey, E.S.I., Al-Lawati, H. and Al-Sumri, A.S. (2012), "Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date palm leaflets", *J. Environ. Sci.*, **24**(9), 1579-1586. [https://doi.org/10.1016/S1001-0742\(11\)60949-2](https://doi.org/10.1016/S1001-0742(11)60949-2).
- El Nemr, A., Aboughaly, R.M., El Sikaily, A., Ragab, S., Masoud, M.S. and Ramadan, M.S. (2020), "Microporous nano-activated carbon type I derived from orange peel and its application for Cr(VI) removal from aquatic environment", *Biomass Convers. Biorefinery*, 1-19. <https://doi.org/10.1007/s13399-020-00995-5>.
- Fernandez, M.E., Nunell, G.V., Bonelli, P.R. and Cukierman, A.L. (2014), "Activated carbon developed from orange peels: Batch and dynamic competitive adsorption of basic dyes", *Ind. Crop. Prod.*, **62**, 437-445. <https://doi.org/10.1016/j.indcrop.2014.09.015>.
- Foo, K.Y. and Hameed, B.H. (2012), "Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K₂CO₃ activation", *Bioresour. Technol.*, **104**, 679-686. <https://doi.org/10.1016/j.biortech.2011.10.005>.
- Freundlich, H.M.F. (1906), "Over the adsorption in solution", *J. Phys. Chem.*, **57**, 385-471.
- Ganesan, S., Amirthalingam, M., Arivalagan, P., Govindan, S., Palanisamy, S., Lingassamy, A.P. and Ponnusamy, V.K. (2019), "Absolute removal of ciprofloxacin and its degraded byproducts in aqueous solution using an efficient electrochemical oxidation process coupled with adsorption treatment technique", *J. Environ. Manage.*, **245**(100), 409-417. <https://doi.org/10.1016/j.jenvman.2019.05.092>.
- Gao, Y., Yue, Q., Gao, B. and Sun, Y. (2015), "Optimization preparation of activated carbon from *Enteromorpha prolifera* using response surface methodology and its adsorption studies of fluoroquinolone antibiotics", *Desalin. Water Treat.*, **55**(3), 624-636. <https://doi.org/10.1080/19443994.2014.922442>.
- Githinji, L.J.M., Musey, M.K. and Ankumah, R.O. (2011), "Evaluation of the fate of ciprofloxacin and amoxicillin in domestic wastewater", *Water Air Soil Pollut.*, **219**(1-4), 191-201. <https://doi.org/10.1007/s11270-010-0697-1>.
- Ho, Y.S., McKay, G. (1999), "Pseudo-second order model for sorption processes", *Proc. Biochem.*, **34**, 451-465.
- Huang, L., Wang, M., Shi, C., Huang, J. and Zhang, B. (2014), "Adsorption of tetracycline and ciprofloxacin on activated carbon prepared from lignin with H₃PO₄ activation", *Desalin. Water Treat.*, **52**(13-15), 2678-2687. <https://doi.org/10.1080/19443994.2013.833873>.
- Igwegbe, C.A., Oba, S.N., Aniagor, C.O., Adeniyi, A.G. and Ighalo, J.O. (2021), "Adsorption of ciprofloxacin from water: A comprehensive review", *J. Ind. Eng. Chem.*, **93**, 57-77. <https://doi.org/10.1016/j.jiec.2020.09.023>.
- Imamoglu, M., Şahin, H., Aydın, Ş., Tosunoğlu, F., Yılmaz, H. and Yıldız, S.Z. (2016), "Investigation of Pb(II) adsorption on a novel activated carbon prepared from hazelnut husk by K₂CO₃ activation", *Desalin. Water Treat.*, **57**(10), 4587-96. <https://doi.org/10.1080/19443994.2014.995135>.
- Imamoglu, M., Ozturk, A., Aydın, Ş., Manzak, A., Gündoğdu, A. and Duran, C. (2018), "Adsorption of Cu(II) ions from aqueous solution by hazelnut husk activated carbon prepared with potassium acetate" *J. Disper. Sci. Technol.*, **39**(8), 1144-1148. <https://doi.org/10.1080/01932691.2017.1385479>.
- Kiraz, A., Canpolat, O., Erkan, E.F. and Özer, C. (2019), "Artificial neural networks modeling for the prediction of Pb(II) adsorption", *Int. J. Environ. Sci. Technol.*, **16**(9), 5079-5086. <https://doi.org/10.1007/s13762-018-1798-4>.
- Lagergren, S. (1898), "About the theory of so-called adsorption of soluble substances", *Kungliga Svenska Vetenskapsakademiens Handlingar*, **24**, 1-39.
- Lam, S.S., Liew, R.K., Wong, Y.M., Yek, P.N.Y., Ma, N.L., Lee, C.L. and Chase, H.A. (2017), "Microwave-assisted pyrolysis with chemical activation, an innovative method to convert orange peel into activated carbon with improved properties as dye adsorbent", *J. Clean. Prod.*, **162**, 1376-1387. <https://doi.org/10.1016/j.jclepro.2017.06.131>.
- Langmuir, I. (1918), "The adsorption of gases on plane surfaces of glass, mica and platinum", *J. Am. Chem. Soc.*, **40**(9), 1361-1403.
- Maheshwari, M., Vyas, R.K. and Sharma, M. (2013), "Kinetics, equilibrium and thermodynamics of ciprofloxacin hydrochloride removal by adsorption on coal fly ash and activated alumina", *Desalin. Water Treat.*, **51**(37-39), 7241-7254. <https://doi.org/10.1080/19443994.2013.775076>.
- Mansour, F., Al-Hindi, M., Yahfoufi, R., Ayoub, G.M. and Ahmad, M.N. (2018), "The use of activated carbon for the removal of pharmaceuticals from aqueous solutions: A review", *Rev. Environ. Sci. Biotechnol.*, **17**(1), 109-145. <https://doi.org/10.1007/s11157-017-9456-8>.
- Mekhamer, W. and Al-Tamimi, S. (2019), "Removal of ciprofloxacin from simulated wastewater by pomegranate peels", *Environ. Sci. Pollut. Res.*, **26**(3), 2297-2304. <https://doi.org/10.1007/s11356-018-3639-x>.
- Mohammed, A.A., Al-Musawi, T.J., Kareem, S.L., Zarrabi, M. and Al-Ma'abreh, A.M. (2019), "Simultaneous adsorption of tetracycline, amoxicillin, and ciprofloxacin by pistachio shell powder coated with zinc oxide nanoparticles", *Arab. J. Chem.*, **13**(3), 4629-4643. <https://doi.org/10.1016/j.arabjc.2019.10.010>.
- Mondal, S.K., Saha, A.K. and Sinha, A. (2018), "Removal of ciprofloxacin using modified advanced oxidation processes: Kinetics, pathways and process optimization", *J. Clean. Prod.*,

- 171, 1203-1214. <https://doi.org/10.1016/j.jclepro.2017.10.091>.
- Movasaghi, Z., Yan, B. and Niu, C. (2019), "Adsorption of ciprofloxacin from water by pretreated oat hulls: Equilibrium, kinetic, and thermodynamic studies", *Ind. Crop Prod.*, **127**, 237-250. <https://doi.org/10.1016/j.indcrop.2018.10.051>.
- Munagapati, V.S. and Kim, D.S. (2016), "Adsorption of anionic azo dye Congo Red from aqueous solution by Cationic Modified Orange Peel Powder", *J. Mol. Liq.*, **220**, 540-548. <https://doi.org/10.1016/j.molliq.2016.04.119>.
- Neimark, A.V. (1995), "In FundamentaZs ofInhomogeneous Fluids", *J. Chem. Soc., Faraday Trans.*, **11**(1), 2857.
- Ozer, C. (2020), "Kinetic and equilibrium studies on the batch removal of methylene blue from aqueous solution by using natural magnetic sand", *Desalin. Water Treat.*, **201**, 393-403. <https://doi.org/10.5004/dwt.2020.26204>.
- Öztürk, N., Yazar, M., Gündoğdu, A., Duran, C., Şentürk, H. B. and Soylak, M. (2021), "Application of cherry laurel seeds activated carbon as a new adsorbent for Cr(VI) removal", *Membr. Water Treat.*, **12**(1), 11-21. <https://doi.org/10.12989/mwt.2021.12.1.011>.
- Palacio, D.A., Rivas, B.L. and Urbano, B.F. (2018), "Ultrafiltration membranes with three water-soluble polyelectrolyte copolymers to remove ciprofloxacin from aqueous systems", *Chem. Eng. J.*, **351**(0), 85-93. <https://doi.org/10.1016/j.cej.2018.06.099>.
- Peñafiel, María E., Matesanz, J.M., Vanegas, E., Bermejo, D., Mosteo, R. and Ormad, M.P. (2021), "Comparative adsorption of ciprofloxacin on sugarcane bagasse from Ecuador and on commercial powdered activated carbon", *Sci. Total Environ.*, **750**. <https://doi.org/10.1016/j.scitotenv.2020.141498>.
- Peñafiel, M.E., Vanegas, E., Bermejo, D., Matesanz, J.M. and Ormad, M.P. (2019), "Organic residues as adsorbent for the removal of ciprofloxacin from aqueous solution", *Hyperfine Interact.*, **240**(1). <https://doi.org/10.1007/s10751-019-1612-9>.
- Peng, X., Hu, F., Zhang, T., Qiu, F. and Dai, H. (2018), "Amine-functionalized magnetic bamboo-based activated carbon adsorptive removal of ciprofloxacin and norfloxacin: A batch and fixed-bed column study", *Bioresource Technol.*, **249**, 924-934. <https://doi.org/10.1016/j.biortech.2017.10.095>.
- Pua, F.L., Sajab, M.S., Chia, C.H., Zakaria, S., Rahman, I.A. and Salit, M.S. (2013), "Alkaline-treated cocoa pod husk as adsorbent for removing methylene blue from aqueous solutions", *J. Environ. Chem. Eng.*, **1**(3), 460-465. <https://doi.org/10.1016/j.jece.2013.06.012>.
- Ravikovitch, P.I. and Neimark, A.V. (2001), "Characterization of micro- and mesoporosity in SBA-15 materials from adsorption data by the NLDFT method", *J. Phys. Chem. B*, **105**(29), 6817-6823. <https://doi.org/10.1021/jp010621u>.
- Sayın, M., Can, M., Imamoglu, M. and Arslan, M. (2017), "Highly efficient adsorption of Rh(III) from chloride containing solutions by triazine polyamine polymer", *Water Air Soil Pollut.*, **228**(3). <https://doi.org/10.1007/s11270-017-3284-x>.
- Usanmaz, S., Özer, C. and İmamoğlu, M. (2021), "Removal of Cu(II), Ni(II) and Co(II) ions from aqueous solutions by hazelnut husks carbon activated with phosphoric acid", *Desalin. Water Treat.*, **227**, 300-308. <https://doi.org/10.5004/dwt.2021.27303>.
- Wang, M., Li, G., Huang, L., Xue, J., Liu, Q., Bao, N. and Huang, J. (2017), "Study of ciprofloxacin adsorption and regeneration of activated carbon prepared from Enteromorpha prolifera impregnated with H₃PO₄ and sodium benzenesulfonate", *Ecotox. Environ. Safe.*, **139**, 36-42. <https://doi.org/10.1016/j.ecoenv.2017.01.006>.
- Wang, Y.X., Ngo, H.H. and Guo, W.S. (2015), "Preparation of a specific bamboo based activated carbon and its application for ciprofloxacin removal", *Sci. Total Environ.*, **533**, 32-39. <https://doi.org/10.1016/j.scitotenv.2015.06.087>.
- Zhang, B., Han, X., Gu, P., Fang, S. and Bai, J. (2017), "Response surface methodology approach for optimization of ciprofloxacin adsorption using activated carbon derived from the residue of desilicated rice husk", *J. Mol. Liq.*, **238**, 316-325. <https://doi.org/10.1016/j.molliq.2017.04.022>.
- Zhang, C.L., Qiao, G.L., Zhao, F. and Wang, Y. (2011), "Thermodynamic and kinetic parameters of ciprofloxacin adsorption onto modified coal fly ash from aqueous solution", *J. Mol. Liq.*, **163**(1), 53-56. <https://doi.org/10.1016/j.molliq.2011.07.005>.

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