

Article

Investigation of Direct Applicability of Modified Agricultural Waste for Contaminant Removal from Real Textile Wastewater

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Abstract: The textile industry produces enormous volumes of wastewater which must be treated effectively. In this study, biosorbent from the agricultural waste of potato peels (PP), which is environmentally friendly and easy to find everywhere, was used for the treatment of real textile wastewater. Physical modification, chemical activation, bio-hybrid and high-pressure modification processes were applied to PP to investigate the organic pollutant removal (chemical oxygen demand (COD)) and inorganic (Fe^{2+} , Ni^{2+} , Cu^{2+} and Cd^{2+}) from original textile wastewater. Additionally, the effects of contact time (5, 15, 30, 60, 120, and 1440 min) and particle sizes (1.5–1.0 mm, 1.0–0.5 mm, and smaller than 0.5 mm in diameter) were investigated in a batch treatment system. Application of the physical modification process to PP presented an attractive solution for COD removal efficiency (69.50%) and removal efficiencies for four divalent metal ions; 78.6% for Cu^{2+} , 63.6% for Ni^{2+} , 40% for Fe^{2+} , and 34.6% for Cd^{2+} . FT-IR, SEM, and EDX analysis were performed to reveal the adsorption mechanism of the modified adsorbents. The FT-IR results indicate that the adsorption process fits the chemical and physical removal mechanisms, which were also supported by SEM images and EDX results.



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1. Introduction

The textile industry, one of the most seasoned business sectors, is an important component for the economy of many countries, especially developing countries [1]. However, 20% of water pollution in the world is caused by the textile industry, according to the World Bank. Generally, these wastes include suspended solids (SS), phosphates, dyes, salts, organo-pesticides, non-biodegradable organics, and heavy metals [2].

Heavy metals, one of the major contaminants in the ecosystem, cause deterioration of environmental quality. When insufficiently treated wastewaters are used for irrigation, crops can uptake heavy metals from their roots into different parts and heavy metals accumulate the body of the plant. Living organisms require a small concentration of some heavy metals such as copper, iron, etc. [3,4]. However, concentrations can increase through the food chain, causing critical human and environmental health problems [5,6]. Also, heavy metals can be transported from their sources by flowing water [4]. For all of these reasons, heavy metals in wastewaters must be treated before discharging into the ecosystem. The treatment process should be cost-effective for implementation in developing countries. For the removal of heavy metals from aqueous solutions, adsorption processes are a more cost-effective technique than most common techniques (chemical process, electrochemical etc.) and suitable for use at low concentrations [7]. Investigation of low-cost sorbents with high metal binding capacities and sustainability has been performed by researchers [6]. Due to cost-effective sorbents, most agricultural waste types (jackfruit, maize cob, pecan shell, hazelnut shell, rice husk, etc.) have been investigated. These were commonly indicated to have small adsorption ability, which in common sense terms requires that large amounts are needed, rendering their application unfeasible. For these reasons, forms modified

chemically [8,9], thermally [10], and biologically (immobilizing matrix including plant waste materials and microbial biomass) [11] have been examined.

Potatoes are the main diet for developing countries after rice and wheat due to including mineral, vitamins, antioxidants and polysaccharides, such as starch, cellulose, hemicellulose, lignin, and fermentable sugars [12]. With the increasing population of the world, the consumption of potatoes has also increased. A large volume of potato peel (PP) is commonly thrown away in landfills, which cause pollution owing to microbial spoilage [12]. Therefore, this waste has generated interest for environmentally-friendly usage such as producing energy (bioethanol etc.) [12] and as adsorbent [10,13–16]. This not only prevents pollution but also provides a low-cost material.

PP has been evaluated for its capacity to remove heavy metals such as Cu^{2+} [17]. To make it more effective, modified PPs have also been examined by researchers. For instance, activated carbon produced by pyrolysis of PP, activation with chemicals, and PPs charcoal was investigated for the removal of Co^{2+} [18] and Cu^{2+} from aqueous solutions [10,13], respectively. PP was selected as an adsorbent by most researchers even though employing activated carbon from wood or coal as adsorbent material provided encouraging results for treatment, as they are usually moderately expensive in developing countries due to their manufacturing production [18].

As mentioned above, up to now, PPs have been tested as a potential adsorbent for the treatment of heavy metals. However, the adsorption process in the literature commonly used a single metal sorption system. Research about adsorption capacities for the removal of a few heavy metals which have different concentrations in the same aqueous solutions are still lacking, but would provide novel aspects in the approach to this issue. Hence, it is very interesting to investigate the removal capacities of more than one heavy metal species in original textile wastewater by modified PPs. Special consideration is given to applicable methods as cost-effective modification techniques and cost-effective treatment methods for developing countries.

The purpose of the study was to investigate the efficacy of four different pretreatments (the physical modification process, chemical activation process, bio-hybrid process, and high-pressure modification process) of PP, which is an environmentally friendly and sustainable adsorbent, to observe the effect of operating parameters on the removal of organic and inorganic (Fe^{2+} , Ni^{2+} , Cu^{2+} and Cd^{2+}) pollutants from real denim industry wastewater containing multiple pollutants. Additionally, fourier-transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and energy-dispersive X-ray spectroscopy (EDX) analyses were applied to the adsorbent materials to better reveal the role of the modification mechanism on the adsorption process.

2. Materials and Methods

2.1. Biosorbent Preparation

Potatoes, obtained from a local farm in Van, Turkey, were washed carefully until the removal of particles was achieved. After peeling the potatoes, the peels were repeatedly washed with deionized water and left for approximately 3 h in water. The washed peels were dried at room temperature and then put in an oven at 115 °C for 24 h [14] before storage at room temperature. Some dried products were separated and named non-modified potato peel, indicated as “Non-MPP”. Matest Sieve Shaker was used to achieve uniform particle sizes of 1.5–1 mm, 1–0.5 mm, and smaller than 0.5 mm. These sieve plates were positioned in new and spotless polypropylene flasks. These samples were called PP modified by a physical process or “MPP-P”. To thermally modify the PP, some of the 1.5–1-mm size portion MPP-P was treated with pressurized saturated steam at 121 °C for 20 min (NÜVE NC 40M, Ankara, Turkey) (autoclave process). This was named PP modified by the high-pressure modification process (MPP-A). To chemically activate PP, another sample of the 1.5–1-mm size portion of MPP-P was soaked in an alkaline solution (0.1 N NaOH) for 1 h and then washed with double distilled water prior to drying at 80 °C (NÜVE FN500P, Ankara, Turkey) overnight. This was labelled as PP modified by a chemical

(MPP-C). Another sample of the 1.5–1 mm size (MPP-P) was combined with *Saccharomyces cerevisiae* as it is easily obtained from different sustenance and beverage industries and is an effective biosorbent in a single system [19] to make hybrid biosorbent. Yeast solution with 3 mL, which was prepared from 20 g commercial instant dry yeast (Pakmaya Company, Istanbul, Turkey) and L-sterilized water, was added to vessels containing 0.5 g MPP-P in 15 mL sterile water. The vessels were shaken for 18 h with an Orbital Shaker (JSR, JSOS-700 Gongju-City, Republic of Korea) (100 rpm at room temperature). After the shaking process, the pretreated sorbents were dried at 80 °C (NÜVE FN500P, Ankara, Turkey). The resulting substance is referred to as bio-hybrid PPs (MPP-Y) in this research.

2.2. Analysis of Samples

During the experiments, glass materials were washed with 20% nitric acid and deionized water to effectively clean the laboratory material and then were dried at 383 K for 1 h [13].

The original textile wastewater was obtained from a local textile industry and the sample was preserved according to standard methods [20]. Characteristics of the textile wastewater were also determined according to the standard method. The COD value of the wastewater was measured with the closed reflux (colorimetric) method (Standard Method 5220D). The physicochemical properties (salinity, conductivity, pH, and total dissolved solids (TDS)) and total organic carbon (TOC) in the wastewater were analyzed using a water quality meter (AZ86505, Taichung City 427, Taiwan R.O.C) and TOC Shimadzu TOC-L analyzer (Kyoto, Japan), respectively. The heavy metal analysis was carried out with Furnace Atomic Absorption Spectrophotometer (Thermo Scientific, iCE-3000 series, Waltham, MA, USA) at the Central Research Laboratory of Van Yüzüncü Yıl University.

Scanning electron microscopy (SEM) (ZEISS Sigma 300, White Plains, NY 10601, USA), energy-dispersive x-ray spectroscopy (EDX) (ZEISS Smart EDX, White Plains, NY 10601, USA) analyses and Fourier Transform Infrared Spectroscopy (FT-IR) analyses (Thermo Fisher Scientific brand, Nicolet IS 10 model spectrometer, Waltham, MA, USA) were performed to characterize the adsorbents.

2.3. Batch Sorption Studies

Experiments were performed with 0.5 g of adsorbents; MPP-P, MPP-A, MPP-C, MPP-Y, and Non-MPP, with 150 mL of the original textile wastewater in Erlenmeyer flasks. All experiments were conducted with fixed agitation rate of 150 rpm (Orbital Shaker, JSR, JSOS-700) at a room temperature of 25 °C. This research targeted the removal of contaminants in the textile wastewater based on an efficient type of sorbent with a low-cost production process for developing countries.

To understand the removal efficiency of the organic contaminants in the wastewater, the COD values were measured for raw wastewater and wastewaters treated after 1440 min of reaction time.

Heavy metal adsorption capacity was also investigated for different contact times such as 0, 5, 15, 30, 60, 120, and 1440 min. At the end of the experiments, the wastewater in the vessels was centrifuged at 9000 rpm for 10 min (NÜVE NF800R, Ankara, Turkey) and then filtered with 0.45 µm syringe filters. The supernatant was prepared based on a study by Nzediegwuand et al. for divalent ion analysis [5].

2.4. Analysis

Each trial was performed in triplicate. The results are shown as averages to ensure quality assurance. Microsoft Excel was used for the calculation of average values and standard deviation for all investigated analyses. The removal efficiency for COD, TDS, and heavy metals was calculated according to Equation (1).

$$\% \text{ Removal Efficiency} = (C_o - C_t) / C_o \times 100, \quad (1)$$

C_0 and C_t are the initial concentration and concentration at t time (for each parameter; COD (mg/L), TDS (mg/L) and Fe, Ni, Cu, and Cd (mg/L)) in the wastewater.

Regarding time t , the adsorption capacity of PPs was obtained from:

$$q_t \text{ (mg/g)} = [(C_0 - C_t)V]/m, \quad (2)$$

where V is the volume of the solution (L), and m is the amount of sorbent (g).

3. Results and Discussion

3.1. Properties of Original Textile Wastewater

The values of pH, conductivity, salinity, TDS, COD, and TOC in the wastewater are shown in Table 1. These values are relatively compatible to descriptions in the literature [21–23]. The concentrations of metal ions in the wastewater followed the order of $\text{Ni} > \text{Fe} > \text{Cu} > \text{Cd}$, and were 2.2 ± 0.03 mg/L, 1.20 ± 0.40 mg/L, 0.10 ± 0.01 mg/L, 0.07 ± 0.01 mg/L, respectively.

Table 1. Characteristics of local textile wastewater.

Parameters	Average $\pm$ SD ¹
pH	9.44 ± 0.56
Conductivity ($\mu\text{S}/\text{cm}$)	1506.5 ± 53.5
Salinity (ppt)	0.775 ± 0.02
TDS (mg/L)	753.5 ± 26.5
COD (mg/L)	1727.5 ± 52.5
TOC (mg/L)	2515 ± 76

¹ Standard Deviation.

3.2. Effect of Particle Size on Adsorption Performance

When the adsorbent surface is increased, the contaminant has more area for adsorption; therefore, the removal efficiency of the contaminant increases when small pieces of an adsorbent are used. However, the COD removal efficiency in the research was calculated to be higher for the 1.5–1 mm particle size of the MPPs than for the smaller particle size of MPPs (Table 2). The reason may be related to some organic matters (starch etc.) releasing water from the peels. Another surprising result was found for TDS values. The values of the effluents were found to be more than the influent. It can be concluded that MPP may release some carbohydrate, such as sugar or starch, into the water as reported by Şapcı Ayas et al. [24]. Therefore, the removal capacity of the organic material in the original wastewater is lower for the small particles of MPPs than for large particle MPPs.

Table 2. Removal ratios of COD and TDS and correlation between TDS and EC (electrical conductivity) for different particle sizes (Reaction temperature of 25 °C, agitation speed of 150 rpm and the reaction time of 24 h).

Sample Names	COD Removal Efficiency (%)			TDS Removal Efficiency (%)			Regression Equation		
Non-MPP	n.a ¹			−14.10			TDS = 0.50 × EC		
	Particles Size (mm)			Particles Size (mm)			Particles Size (mm)		
	1.5–1.0	1.0–0.5	<0.5	1.5–1.0	1.0–0.5	<0.5	1.5–1.0	1.0–0.5	<0.5
MPP-P	69.50	75.44	65.67	11.15	11.54	11.54	TDS = 0.50 × EC	TDS = 0.50 × EC	TDS = 0.50 × EC
MPP-A	44.46	31.12	33.58	−11.92	−13.72	−15.00	TDS = 0.50 × EC	TDS = 0.50 × EC	TDS = 0.50 × EC
MPP-C	54.71	53.78	34.40	−11.03	−12.56	−34.40	TDS = 0.50 × EC	TDS = 0.50 × EC	TDS = 0.50 × EC
MPP-Y	49.24	32.10	57.52	−14.10	−14.74	−16.41	TDS = 0.50 × EC	TDS = 0.50 × EC	TDS = 0.50 × EC

¹ not available.

Dissolved ions and their types affected correlations between TDS and EC [25]. Investigations about the correlation between TDS and EC showed that coefficient values for untreated wastewater and all treated effluents (Table 2) were calculated to be the same at 0.50. Youcai and Sheng reported that the TDS and EC correlation for metropolitan

wastewater was 0.55, even though the values for ordinary water and urban water were 0.54 and 0.60, respectively [26]. Correlations between EC and TDS in natural waters taken from areas polluted by textile effluent were determined to be between 0.59 and 0.93 [25].

3.3. Effect of Contact Time on Heavy Metals Adsorption Performance

The metal removal percentages for each adsorbent showed the same increasing trend at the beginning of the trial. The impact of contact time on adsorption implementation was linked to the number of dynamic adsorption sites on the adsorbent. In the beginning stage, many active binding sites were empty; the adsorbent gained metals by electrostatic attraction effectively. During the contact time, a huge quantity of metals were adsorbed, and most of the adsorption sites and pore spaces were involved, which weakened the metal adsorption capacity of the adsorbent [27,28]. Therefore, the beginning of all the trials in this research showed the removal percentages for all investigated metals increased rapidly (Figure 1).

The amounts of adsorption, except for Cu^{2+} ion, on the MPPs were higher than for Non-MPP (Figure 1). Possibly, Fe^{2+} , Ni^{2+} , and Cd^{2+} ions do not have enough affinity to the adsorption sites of the Non-MPP and are disposed to stay in water rather than being adsorbed by the Non-MPP. Similarly, Feizi and Jalali [15] reported that sorption of Ni by activated sorbent by NaOH was higher than for native sorbent. Another study indicated that H^+ ions in the water reacted with functional groups on PP choral surface due to the limitation of the number of Cu^{2+} binding sites [13]. Additionally, competitive sorption mechanisms were observed in the process possibly due to presence of four different types of heavy metals (Cu^{2+} , Ni^{2+} , Fe^{2+} , Cd^{2+}) in the original wastewater. It can be concluded that the MPPs have specific sites for Ni^{2+} , Fe^{2+} and Cd^{2+} . In addition, the ionic radii of these heavy metals may be also a factor for increasing the amounts of adsorption on the MPPs. For Cu^{2+} , Ni^{2+} , Fe^{2+} , and Cd^{2+} this is reported to be 0.73 Å, 0.69 Å, 0.64 Å, and 0.97 Å, respectively [15]. When the ionic radius increased, no relationship was observed between the removal percentage of the heavy metals and their ionic radii, consistent with the results of Feizi and Jalali [15]. In the light of all this information, after the modification process, these MPPs probably have more affinity with pores, which caused higher removal percentages for these metals from the wastewater. The high removal percentage of these metals probably takes time to equilibrate due to more pores on the modified adsorbents than the non-modified adsorbent.

Figure 1 indicates that the Cu^{2+} removal percentage was higher than the other investigated heavy metals for all MPPs and Non-MPP. The minimum removal percentage for Cu^{2+} was determined to be 70% at the MPP-C trial, which showed similar trends to the removal percentages for Ni^{2+} and the Cd^{2+} . Comparing contact time and adsorbent type, the Cu^{2+} removal efficiency with MPP-P needed more time than other adsorbents. The removal percentages for Fe^{2+} , Ni^{2+} , and Cd^{2+} with MPP-P increased in the first 5 min, but later their removal percentages reduced, while the Cu^{2+} removal percentage increased hastily until 30 min and then increased slowly from 30 min to 1440 min (Figure 1B). Van der Waals forces were weak to the process. In spite of their weak bonds, they play an important role in adsorption mechanisms [6,29]. The reason for the increasing removal percentages for Fe^{2+} , Ni^{2+} , and Cd^{2+} at the beginning followed by small fluctuations was probably related to the van der Waals forces.

The effect of contact time on Cd^{2+} removal by all adsorbents showed the same trend at the beginning, but later percentages decreased starting in the 60th min for the Non-MPP trial and in the 15th min for the MPP-Y trial (Figure 1A,E). The Non-MPP trial also showed that from the moment of the Cd^{2+} removal the percentage decreases; the Fe^{2+} removal percentages increased more than the Cu^{2+} removal percentage. The MPP-Y trial indicated that the removal percentage of not only Cd^{2+} but also Fe^{2+} decreased after the 15th min of the trial. On the other hand, while the Cd^{2+} removal percentage decreased until 1440 min, the Fe^{2+} removal percentages decreased to 120 min and then increased again. Between the 15th min and 120th min of the trial, it was observed that the Ni^{2+} removal percentages

fluctuated as they increased from the beginning to the 120th min of the trial and then decreased. In this decreasing period for Ni^{2+} , Fe^{2+} removal percentages increased slightly again (Figure 1E). As seen in Figure 1C, the variations in metal percentages for the MPP-A showed that when Cd^{2+} removal percentage increased, Fe^{2+} removal percentage decreased (Figure 1C). Cd^{2+} and Fe^{2+} are -0.40 E and -0.44 E, respectively, which might affect antagonist adsorption during this adsorption process.

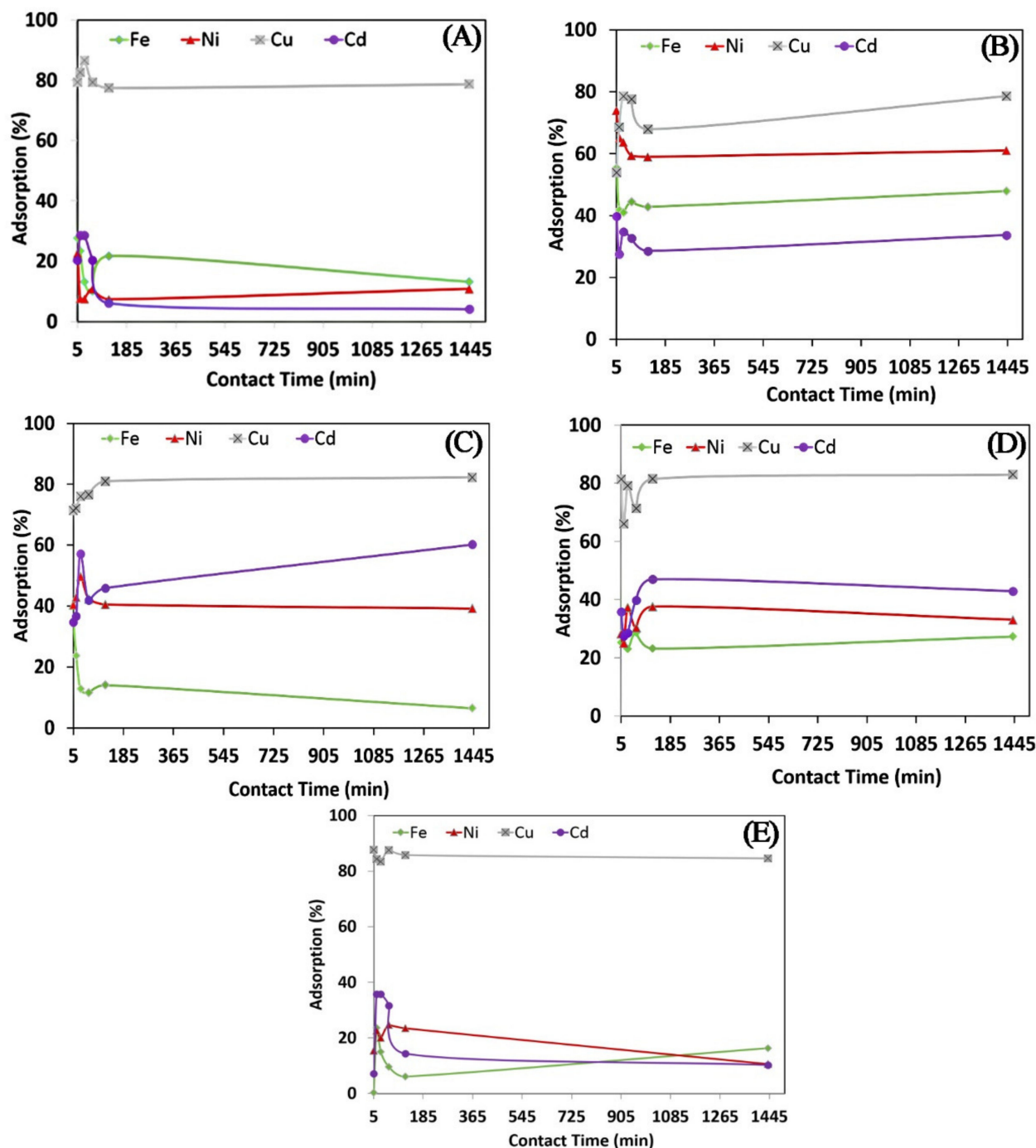


Figure 1. Effect of contact time on Fe^{2+} , Ni^{2+} , Cu^{2+} , and Cd^{2+} removal percentages with Non-MPP (A), MPP-P (B), MPP-A (C), MPP-C (D), MPP-Y (E).

Ouyang et al. reported that the adsorption amount displayed a significant difference between single metal and multi-metal ion adsorbed on a sorbent due to competition for the

adsorption sites [28]. Examination of the interaction between heavy metal ions and Non-MPP and MPPs adsorbents is important, since several heavy metal ions exist together in the original wastewater. Not only several ions but also variable concentrations of metals are included in the original wastewaters. In this research, the concentrations of metal ions in the original textile wastewater followed the order of $\text{Ni} > \text{Fe} > \text{Cu} > \text{Cd}$. 23.4% of Fe^{2+} , 7.5% of Ni^{2+} , 82.6% of Cu^{2+} , and 28.5% of Cd^{2+} were removed from the original wastewater by Non-MPP ($t = 15$ min) (Figure 1A). Ouyang et al. reported that higher metal concentrations in wastewater ensured strong competition with other ions [28]. In this research, the Ni^{2+} concentrations were higher in the original wastewater compared to others; however, their removal percentage was less than for other metals. Their adsorption efficiency was not the same, which probably depends on differences in the properties of heavy metal ions (ionic potential, electronegativity, etc.) [28]. Comparing the investigated metal removal by Non-MPP with MPP-P ($t = 30$ min), the removal percentages for Fe^{2+} (from 23.4% to 41%), Ni^{2+} (from 7.5% to 63.6%), and Cd^{2+} (from 28.5% to 34.6%) increased, while the efficiency for Cu^{2+} (from 82.6% to 78.6%) decreased (Figure 1A,B). Similarly, comparison of removal by Non-MPP with by MPP-A ($t = 30$ min) indicated that the percentages of Ni^{2+} and Cd^{2+} increased from 7.5% to 49.7% and from 28.5% to 57.1%, respectively, while the efficiency of Fe^{2+} and Cu^{2+} decreased from 23.4% to 12% and from 82.6% to 75.9%, respectively (Figure 1A,C). Likewise, by comparing removal with Non-MPP and MPP-C ($t = 30$ min), the percentage for Ni^{2+} (from 7.5% to 37.2%) improved, while the efficiency for Cu^{2+} (from 82.6% to 79.1%) decreased (Figure 1A,D). The removal ratios for Ni^{2+} , Cd^{2+} , and Cu^{2+} with Non-MPP, compared with MPP-Y ($t = 30$ min), increased from 7.5% to 20%, from 28.5% to 35.7%, and from 82.6% to 87.5%, respectively (Figure 1A,E). All data shows that using MPPs as adsorbent generally increased the metal removal percentage. The maximum removal percentages were determined for Ni^{2+} , Fe^{2+} , Cu^{2+} , and Cd^{2+} during the MPP-P trial (63.6%), MPP-P trial (41%), MPP-Y trial (87.5%), and MPP-Y trial (35.7%), respectively.

Regarding Figure 1, it can be concluded, generally, that the removal percentage rapidly increased at 5 min then basically balanced after 30 min. To understand the adsorption capacity changes regarding contact time, relative percentage differences between the 5 min and 30 min contact times were examined. As can be seen in Figure 2, when contact time increased from 5 min (Figure 2A) to 30 min (Figure 2B) the adsorption capacities for both Ni^{2+} and Cd^{2+} increased more with 30 min contact than with 5 min contact relative to the sorbents. To compare the adsorption capacities between Non-MPP and MPPs, the time was chosen as 30 min (Table 2). These results showed that even though Ni^{2+} had higher concentration than Fe^{2+} in the wastewater; Fe removal was relatively higher with Non-MPP, MPP-P, and MPP-C (Figure 2B and Table 2). As mentioned above, the heavy metal concentration sequence in the real wastewater from high concentration to low concentration was Fe^{2+} , Cu^{2+} , and Cd^{2+} , respectively. The adsorption capacities for these three metals were also determined to be in the same order for all sorbents (Figure 2B and Table 3).

Table 3. Comparison of adsorption capacity ($q_e = 30$ min).

Adsorbent Type	Adsorption Capacity (mg/g)			
	Fe^{2+}	Ni^{2+}	Cu^{2+}	Cd^{2+}
Non-MPP *	29.64	10.08	12.96	3.06
MPP-P	79.8	57.6	5.16	4.32
MPP-A	29.04	43.8	17.4	6.96
MPP-C	47.64	33.84	14.28	3.6
MPP-Y	6.80	9.24	16.32	4.44

* Non-MPP is accepted as 30 min to make comparisons.

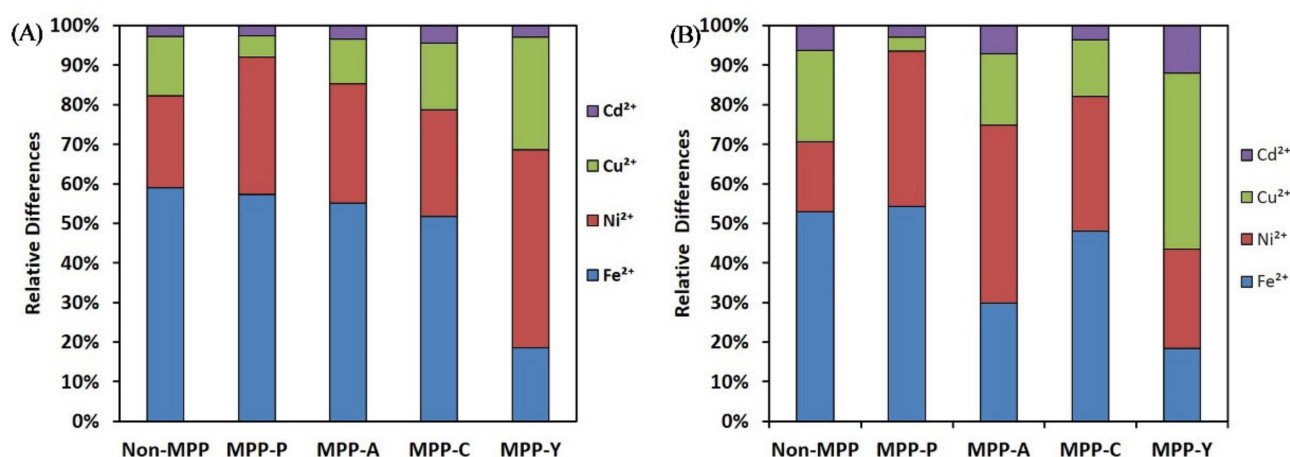


Figure 2. Relative differences in the metal concentrations depend on contact time: 5 min (A) and 30 min (B).

3.4. Analysis of Adsorption Mechanism

FT-IR analysis was carried out on MPP-P and indicated high organic and inorganic removal efficiency after the adsorption process (Figure 3A). To determine the changes in surface functional groups between 4000 to 500 cm^{-1} , functional groups of MPP-P were compared with untreated PP from the literature [17]. Regarding the literature, strong peaks in the spectra of untreated PP were noticed at 3450 cm^{-1} and 2930–2854 cm^{-1} , which indicates the $-\text{OH}$ stretching of the phenol group in cellulose and lignin and $-\text{CH}$ and $-\text{CH}_2$ stretching of an aliphatic compound, respectively. On the spectrum of MPP-P after the adsorption process, the peaks were detected between 3650 and 3000 cm^{-1} for $-\text{OH}$ vibrations and between 2915 and 2850 cm^{-1} for C-H bands, similar to bands in the literature (Figure 3). Other peaks between 1735, 1633, 1515, 1370, and 668 cm^{-1} in Figure 3 were reported for untreated PP by Guechi and Hamdaoui as C=O stretching vibration of the aldehyde group, C=C stretching vibration of phenol group, N-H deformation, C-O-H bending and C-O-H twisting, respectively [17]. The novel peaks noticed after the adsorption process were positioned at 1250 and 1030 cm^{-1} (Figure 3A) and represent the C-O stretching of the guaiacyl unit in lignin and the C-OH stretching vibration of cellulose and hemicellulose, respectively. Moreover, C-O deformation in secondary alcohols and aliphatic ethers were also determined at 1032 cm^{-1} [28]. These peaks observed at 1250 and 1030 cm^{-1} were also reported in FT-IR spectra of PP attained after the Cu^{2+} sorption process [17]. According to the post-adsorption peaks on the FT-IR results, it can be said that the adsorption process fits the chemical and physical removal mechanism.

SEM is commonly used to investigate the morphological structures and physical appearance of adsorbents [17,27]. In the present study, SEM is used to evaluate morphological variations on the PP surfaces following adsorption of Ni^{2+} , Fe^{2+} , Cu^{2+} , and Cd^{2+} . The morphology of the loaded adsorbent provided some important observations. Figure 3B shows the SEM image of MPP-P obtained after the adsorption process. While untreated PP had a rough and porous surface [17], the loaded SEM images show the adsorption of metal ions on the MPP-P (Figure 3B). In Figure 3B depicting the surfaces of particles after adsorption; it is clearly seen that the MPP-P sorbent was covered by metal ions. Based on EDX results, these metal ions were Fe^{2+} , Ni^{2+} , Cu^{2+} , and Cd^{2+} ions (Table 4), which supported the removal of metal ions from the textile wastewater.

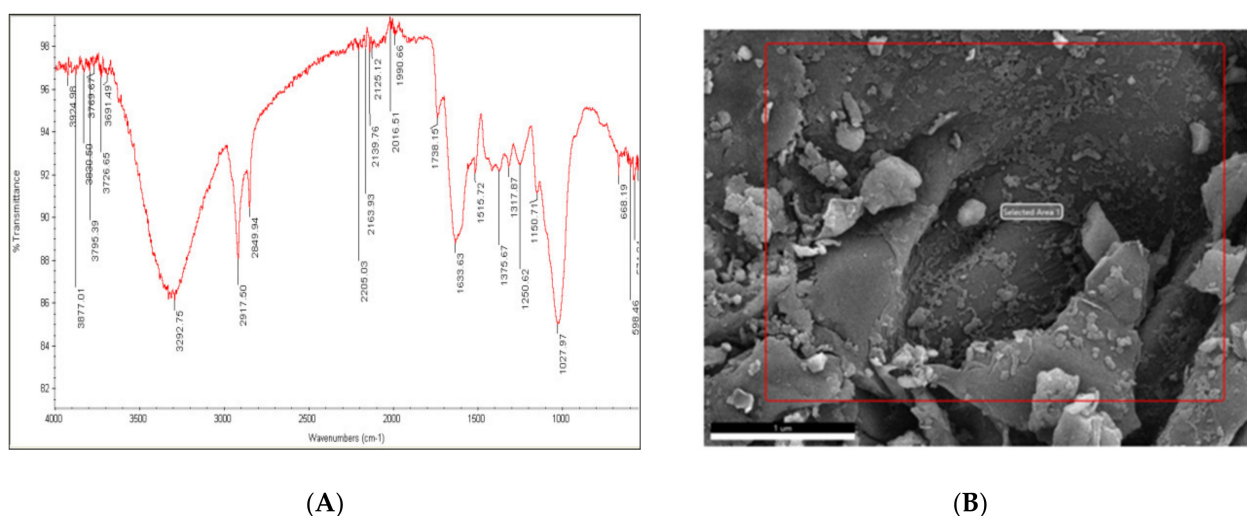


Figure 3. FT-IR Spectra (A) and SEM images of MPP-P obtained after the adsorption process (Mag = 30,000) (B).

Table 4. EDX analysis of SEM images of MPP-P obtained after the adsorption process.

Element	Weight (%)	Atomic (%)
Cd	15.82	9.24
Fe	21.85	25.69
Ni	15.93	17.81
Cu	22.49	23.24
Zn	22.92	24.02

4. Conclusions

This research focused on the prospective use of PP due to its environmentally friendliness and sustainability for the removal of organic components and heavy metals Fe^{2+} , Ni^{2+} , Cu^{2+} , and Cd^{2+} ions, from real textile wastewater. To achieve accurate and sustainable modification of PP, the processes were chosen by considering machinery cost, energy consumption, worker qualifications, etc. Four types of low-cost modification processes, namely the physical modification process, chemical activation process, bio-hybrid process, and high-pressure modification process, were studied. In this study, the heavy metal removal process with all investigated PP happened very rapidly. Based on the COD removal efficiency, particle sizes of 1.5–1.0 mm were suitable, due to sustainability. The removal capacities for heavy metals Fe^{2+} , Ni^{2+} , Cu^{2+} , and Cd^{2+} ions, and COD from real textile wastewater were observed in experiments carried out with MPP-P sorbent. The relative adsorption capacities for the four heavy metals in the study using MPP-P sorbent increased in the order of $\text{Fe}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$. The FT-IR analysis indicated that many functional groups existed on the MPP-P surface.

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