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Design and fabrication of nanocomposite-based polyurethane filter for improving municipal waste water quality and removing organic pollutants

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Abstract
Nanotechnology has been used in different industries for years. In this study, polyurethane filter, modified with nano-sized polypyrrole–ZnO was used for wastewater quality improvement. The effect of coating method and influential parameters on polymer morphology was studied by Fourier transform infrared spectroscopy and scanning electron microscopy. The results revealed that the uniformly synthesized polymers are seed like. The size of synthesized nanoparticles was observed to be about 50–120 nm. The effect of the number of iterative filtration and the height of the filter on improving the quality of the waste water was investigated using central composite design. After filtration, spectroscopy method, gas chromatography method, and some other devices such as biochemical oxygen demand meter and salt meter were used to evaluate the quality of the waste water. The results indicated that the filter efficiency in optimizing parameters such as total dissolved solids, biochemical oxygen demand, chemical oxygen demand, color, salinity, hardness, pH, and organic compounds removal is desirable. After data modeling, the optimal thickness of the filter was 3.8 cm and the most appropriate iteration for filtration was eight times obtained using a graphical method. Results showed that the designed filter had an excellent ability to improve wastewater quality and can be used in water and wastewater refining instruments.

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Nano-structure, polypyrrole–ZnO, filter, waste water, quality improvement

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Introduction

Water is an essential material for life on earth and is a valuable resource for human civilization. Reliable access to clean water with an affordable price is one of the fundamental objectives of human beings and a global challenge in the 21st century. The current supply of water is a huge challenge all over the world. Currently, more than 780 million people around the world do not have access to drinking water resources. Proper and adequate water treatment in developing countries, which often lack the appropriate infrastructure for this purpose, is an inevitable necessity. In developing and industrialized countries, human activities, such as various industries, can play a role in intensifying water shortages by polluting natural resources. The world population is growing rapidly and the standard of living is constantly improving. High pressure on water resources causes the use of unconventional water sources, such as moving water from storms, contaminated fresh water, saline water, wastewater, and sea water, to be taken into consideration. On the other hand, current water and wastewater treatment technologies are developing to provide water quality to meet human and environmental needs (Qu et al., 2013b). Wastewater, basically, is the water consumed by the community, which is contaminated as a result of different applications and not usable for consumption. Of productive resources, wastewater can be considered as a combination of wastage shifted by water from residential, official areas, and commercial and industrial facilities within the city proper, and under the status queue it can be mixed with groundwater, surface water, or floods. Due to the presence of different microbial and chemical contaminants in the waste water, its untreated discharge in the environment or agriculture results in soil, water resources, and agricultural productions pollution and finally, the "harmful to health" hazards affect the health of the person. As estimated, each cubic meter of untreated waste water can contaminate about 40–60 m^3 of fresh water. In order to reduce the harmful effects of sewage discharge into the environment as well as to promote public health in communities, wastewater treatment should be undertaken, which dates back to the second half of the 18th century in England. There are various biological processes to remove or reduce wastewater contaminants, each of which has its own advantages and disadvantages (Li, 2014; Metcalf & Eddy, Inc., 2003; Schwarzenbach et al., 2010). The filtration method in the current state of environmental pollution, especially air pollution, has been widely considered as an effective method for eliminating contamination. In industries, high-performance filtration equipment is also needed as clean technologies (Jackiewicz et al., 2013; Leson and Winer, 1991; Yunus et al., 2012). Due to the global energy crisis and the increase in environmental pollution, the need to use clean and renewable energies and find a way to reduce environmental pollution are more than necessary. Nanotechnology, a nano-scale materials and tool manufacturing technology, has been considered in recent years as a solution to overcome the energy crisis and environmental pollution. Through this technology, the methods of identification, treatment, and purification of pollutants that can greatly contribute to reducing environmental pollution are significantly improved (Kanel et al., 2006; Leupin and Hug, 2005; Li et al., 1999). Therefore, research and implementation of new and safe methods for water disinfection are necessary (Grochowicz et al., 2015). Nanotechnology is a general term that refers to all advanced technologies in the field of nano-scale work (Aslani et al., 2018). Usually, the nano-scale dimension is about 1–100 nm. In fact, nanotechnology knowledge comes from basic elements. Each of these basic elements has certain characteristics, which their use in different fields can create interesting properties. Increasing the area to volume, which gradually occurs by reducing the size of the particle, can overcome the behavior of the atoms located at the particle surface relative to the internal atoms' behavior and increases the surface reactivity of nanoparticles (Heidarpour et al., 2010; Qu et al., 2013).

Vital de Oliveira et al. (2016) in a research studied the molecular modeling of polymer nanocomposites in water and chloroform solvents. Polymer grafting on nanoparticles is an efficient method for obtaining the accumulation, solubility, form, and size of nanoparticles. In this research, a molecular dynamics simulation was conducted to study the polyethylene glycol-based nanocomposite model, in which polymer containing Fe_3O_4 nanoparticles dissolved in water and water and chloroform solvents was carried out. Radial distribution function, dihedral distribution function, the analysis end-to-end distance, and radius of gyration show that the structural property of the polymer in pure form and the form that binds to the nanoparticles are similar. Due to high polymer density, in the presence of chloroform, which is a poor solvent, a compact shell is formed around the surface of the nanoparticles. In the opposite case, in the presence of a good water solvent, due to the entropic effects, polymer chains adopt a broad form of conformation. Furthermore, the polymer structure in the nanocomposite resembles a state considered in solvents. Finally, the results were obtained based on the hypothesis of the transferability of polymer properties to nanoparticles in the solution (Vital de Oliveira et al., 2016).

In a study by Wang et al. (2016), they produced a recoverable titanium dioxide–graphene oxide (TiO_2–GO) composite for treatment of waste water. The production of recyclable composite TiO_2–GO using an ultrasonic method of nanosheets of GO which has been developed by TiO^2 nanoparticles, which overcomes the problems of separating titanium nanoparticles dioxide from the treated water. The separability of prepared samples was systematically examined by gravity settling experiments. The photocatalytic activity of the samples for water disinfection was also studied under the irradiation of a solar simulator. The results indicate that TiO_2–GO showed high-performance separability due to accelerated settling. Generally speaking, the TiO_2–GO composite showed good results for water disinfection (Wang et al., 2016).

Rytwo (2012) used a clay–polymer nanocomposite for wastewater treatment. Some agricultural effluents are unsuitable for discharges at standard wastewater treatment plants, where pretreatment is needed to avoid clogging of colloidal filtering devices. This study presents the use of nanocomposites comprised of particle anchoring and polymers as coago-flocculants for quick reduction of total suspended solid (TSS) and wastewater turbidity with high organic matter is an effective method. The benefits of using such combined particles are to neutralize the charge of suspended particles in the wastewater by bridging between the particles and bridging between denser particles enhances precipitation (Rytwo, 2012).

Ren et al. (2010) designed a novel membrane bioreactor (MBR) with a nonwoven fabric filter for household wastewater treatment. Conventional and modified MBRs are widely used in the treatment of small-scale sewages. However, due to relatively high costs and operational complexity, their widespread applications are blocked. In this study, we have investigated a new concept for wastewater treatment using a nonwoven fabric filter bag (NFFB) as an MBR. Activated sludge was produced in an NFFB by using the filtration with fabric filter through gravity flow without suction pump. This study divulged that the biofilm layer is achieved in a nontextured filter bag of 10 mg/l suspended solids in 20 min initial operations. The dynamic biofilter layer displayed good filterability. Although the reactor provided aerobic conditions, denitrification in the biofilm layer to improve alkalinity and avoid the need for alkalinity supplementation has occurred. This study shows that the NFFB system has a high potential for efficient wastewater treatment with simple costs in rural and sparsely populated areas (Ren et al., 2010).

Azizi et al. (2016) defined effective parameters on the removal of organic materials from the pharmaceutical industry by the advanced oxidation process. Drug wastewater is one of the main compounds and toxic wastes that contain a small amount of biodegradable organic matter. In this study, the main oxidation process of H_2O_2/UV (H_2O_2/UV AOP) is used to remove organic matter from the pharmaceutical industry effluent. Chemical oxygen demand (COD) removal tests have been performed using a medium pressure mercury vapor UV lamp accompanied by hydrogen peroxide. The results indicated that the efficiency of COD removal depends on initial concentration of H_2O_2, oxidation time, and pH (Azizi et al., 2016).

Using nano-structure conductor polymers to remove phenolic compounds, organic, mineral, carcinogenic substances, and degrading compounds from wastewater is the main purpose of this study. The most important pollutants of groundwater, as well as wastewater, are phenolic compounds, organic aromatic, mineral, other carcinogenic, and falsifying and degrading compounds. Common separation techniques such as distillation and liquid–liquid extraction are not applicable because of extra waste production. Therefore, the presentation and application of methods producing a small amount of waste removal and separation and greatly reduce the cost of removing and measuring can be effective. The elimination of phenolic compounds, organic compounds removal, mineral, carcinogenic material, and falsifying and degrading compounds requires high-performance filtration systems or expensive chemicals that can handle these compounds in small amounts at ambient temperature. In this project, the conductive polymer of the polypyrrole–ZnO (PPy–ZnO) was used to modify the polyurethane surface and make polymer filters. PPy is one of the conductive polymers that have been studied as a polymer in many applications. Among various conductive polymers, pyrrole can easily be converted to PPy by electrochemical oxidation or chemical. Polypyrrole has a tight and flexible structure and groups with weak ion exchange functionality. The secondary structure of polymers increases the contact surface of the analyte with the filter, and on the other hand, as polyurethane foams are permeable, the analytes are easily exposed to the provided filters (Chon et al., 2012; Partridge et al., 1997; Zhou et al., 1995). The composites containing conductive polymers are materials composed of conjugated polymers and at least one secondary composition, including organic, mineral, or biologically active species. The conductive polymer composite synthesis with metal oxides such as zinc oxide and other organic materials improves sensitivity, prolonging life, and the ability to detect a wide range of analytes (Campbell et al., 1999; Chougule et al., 2011; Geng et al., 2007; Kemp et al., 1999; Kincal et al., 1998; Li et al., 2012; Machappa and Ambika, 2012; Zhang et al., 2008). The effect of the coating method and the effective parameters on the morphology of the polymer was studied by electron microscopy images. In this study, the investigated parameters are total dissolved solid (TDS), biochemical oxygen demand (BOD), COD, organic compounds removal, color, salinity, hardness, and pH.

Material and methods

Materials and equipment

Materials. In this study, polyester foam coated with PPy–ZnO was used to improve the quality of waste water. The pyrrole monomer was provided by Merk Company and other organic compounds were provided by Aldrich Company. The mentioned compounds were used without repurification. The zinc oxide nanoparticles for PPy–ZnO preparation were provided by Aldrich Company, St Louis, MO, USA. In all the experiments twice distilled water was used for preparing the solution. The polyester foam was provided by Mokarrar Engineering Materials Company, Iran.

Instruments. The following devices were used to analyze water quality. The BOD TRAK device (HACH Company, Austria) was used for BOD measurement. For measuring COD, first of all the samples must be digested, since the chemical digestion of the samples is a prerequisite for calculating COD values. For this purpose, the thermal reactor (DRB 200 of the HACH Company, Austria) was used. For COD readings, the DR 2800 spectrophotometer (Austrian HACH) was used. The pH and TDS-METER (Crison MM 40 device made in Spain) was utilized for measuring TDS. To measure the hardness and color, the 7500 Palintest spectrophotometer (made in the UK) was used and the pH-METER, Crison pH 25 (made in Spain) was applied to measure pH. A manual MT-128 salt meter (made in china) was used for measuring salinity. The gas chromatography system (Agilent7890 A, Wilmington, DE, USA) was used to measure and analyze the organic compounds.

Test method

Methods. To prepare the polyurethane foam, first of all it was washed in the water and then dried at 50°C temperature. To cover the polyurethane foam, 200 ml of distilled water was poured in a 500 ml beaker, and then added a portion of the distilled pyrrole to a concentration of 0.1 molar. The beaker was placed on an electric shaker and shaken for 10 min until the pyrrole was completely dispersed into the water. Then, a zinc oxide powder solution was added to a concentration of 0.05 mol and the solution was shaken for 20 min. The cubic polyurethane foam with dimensions of $5 \times 3 \times 6\ cm^3$ was transferred to the beaker and, using a glass agitator, all the water (with particles of pyrrole and zinc oxide) in the beaker was infiltrated into the foam. In another beaker a solution of Iron(III) chloride ($FeCl_3$) was provided. Finally, while the beaker containing polyurethane foam was on the shaker, the contents of $FeCl_3$ were added slowly into the beaker of foam for 30 min and were infiltrated into the foam. The synthesis reaction of PPy–ZnO was continued in foam for 24 h at ambient temperature. During the synthesis of PPy–ZnO, the solution in the beaker was shaken by a mechanical shaker. After the synthesis reaction of PPy–ZnO composite, the foam coated with PPy–ZnO composite was taken out of the synthetic beaker and squeezed mechanically. Finally, the foam coated with PPy–ZnO in a drying oven was dried at 50°C for 1 h.

Mechanical characteristics of provided filter including strain to break (STB) and tensile strength (TS) were recorded by TAXT Tissue Tester (Plus, Stable Micro Systems UK) and the 98.8% for STB and 10.5 MPa for TS were recorded. To measure the size and morphology of nanoparticles, scanning electron microscopy (SEM) was used. The SEM image was prepared using the LEO 1430VP scanning electron microscope manufactured in Germany

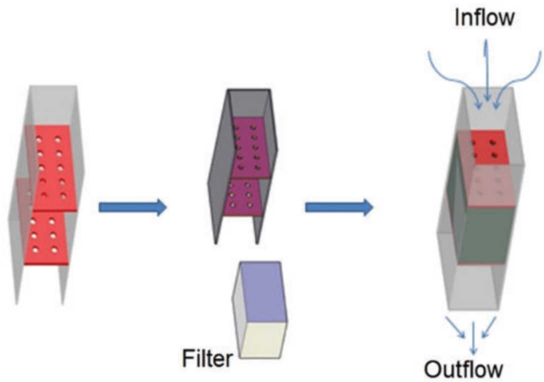

Figure 1. Scheme of the designed filter with the input and output flow.

and England. Investigating the PPy synthesis and synthesized polymers structure, Fourier transform infrared (FT-IR) spectrum was prepared of synthesized polymers. FT-IR images were recorded using the FT-IR spectroscopy, spectrum RXI made in England. After preparing the polyurethane filters with synthesized nanoparticles on the surface, the physical shape of the filter was designed and various parameters such as the length of the filter dimensions were optimized. After designing and optimizing the physical shape and physical parameters, the filter was directly exposed to the water sample at different times and conditions.

Removal percent of contaminants and toxic metals from the water after filtration was investigated by spectroscopy and different devices such as BOD meter and salt meter, etc. In this study, filters 6 cm long and 3 cm wide and different heights 1, 2.5, and 4 cm were used. The schematic shape of the filter is designed as shown in Figure 1. The investigated parameters before and after filtration are color, hardness, salinity, pH, TDS, organic compounds, BOD, and COD.

Statistical analysis. In this study, response surface methodology (RSM) was used for extracting the model and finding the most effective. The RSM is a set of mathematical methods for determining the relationship between one or more response variables with several independent variables. This method was introduced by Box and Wilson in 1951 and still it is used as a design of experiment (Lenth, 2009). This method designates a test matrix by specifying the number of variables and the maximum and minimum limits set for each variable. Thus, the number of tests and the levels of each variable are determined in each test. When the number of variables is high, this method is more effective to the high volume methods such as the factorial. The design of the test is such that even without repeating the test, the statistical results are reliable. Therefore, this method will simplify the research process and reduce time and costs. The central composite design (CCD), Box–Behnken, and Doehlert are the three main methods of designing the response surface. Among these three methods, the CCD is more credible. In this study, for investigating the number of waste water sample passages effect through the filter and the thickness of the filter, the test design is based on the CCD. For this purpose, the effect of two factors of the number of waste water sample passages

Table 1. The variables and values used for central composite design (CCD).

	Coded factor levels		
Variables	Low (−1)	0	High (+1)
A: X_1(iteration)	0	5	10
B: X_2(height (cm))	1	2.5	4

effect through the filter and the filter thickness has been investigated during the 13 different experiments and the optimal test results (the best filter thickness and the best number of waste water sample passages through the filter) is determined. In this test independent variables include the number of passes (X_1) and filter thickness (X_2). For each of the studied variables, a high level (with code +1) and a moderate level (with code 0) and a low level (with code −1) were considered. The information about the level of each of the variables has been demonstrated in Table 1.

The results of statistical analysis were also analyzed using software design-expert-7 and analysis of variance (ANOVA). Using this software, a polynomial mathematical model was proposed for the variables examined to predict the response variables. The optimum conditions for the test variables were determined to minimize or maximize the value of the response variables by this software as well.

Results and discussion

Study of the structure of synthesized polymers

SEM analysis. To investigate the size and morphology of nanoparticles, SEM was used. Figure 2 shows the SEM image of the polyurethane filter, modified by PPy–ZnO. The results indicate that the synthesized polymers are seed like and uniformly synthesized. The size of the synthesized particles is about 50–120 nm.

FT-IR study. Figure 3(a) and (b) shows FT-IR spectrum of PPy and PPy–ZnO particles. Results from FT-IR show that the C–H out-of-plane bending mode is confirmed by 792 and 681 cm^{-1} peaks. The peak at 1049 cm^{-1} assigned vibration of the pyrrole rings. The peaks appearing at 1155 and 1532 cm^{-1} represent C–N stretching vibration and C–C/C=C stretching vibration, respectively (Cheng et al., 2006; Mathys and Truong, 1997; Zhang et al., 2003). The C=O stretching is presented by weak peak at 1690 cm^{-1}. The pyrrole ring is presented by bands at 1612, 1281, and 910 cm^{-1} (Kostić et al., 1995).

In the case of PPy–ZnO the peaks are broadened and often merged and shifted to lower frequency that may be due to some interaction between PPy and ZnO particles. Due to metal oxide bond the peak was observed at lower frequencies from 1319 to 1296, 1172 to 1152, and 1025 to 1005 cm^{-1} with a broad peak at 897 cm^{-1}. These significant changes are corresponding to some chemical interaction between ZnO nanoparticles and PPy (Pirsa et al., 2018; Shukla et al., 2012; Wang et al., 2015).

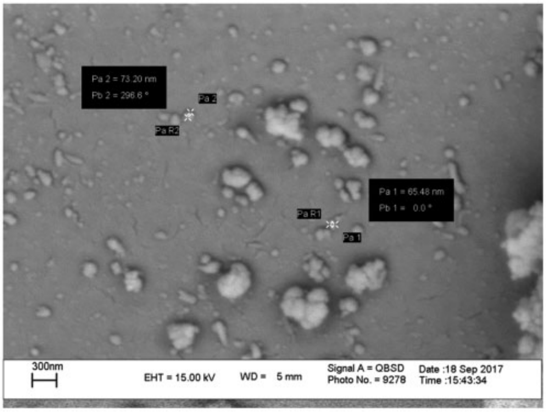

Figure 2. SEM image of polyurethane filter, modified with PPy–ZnO.

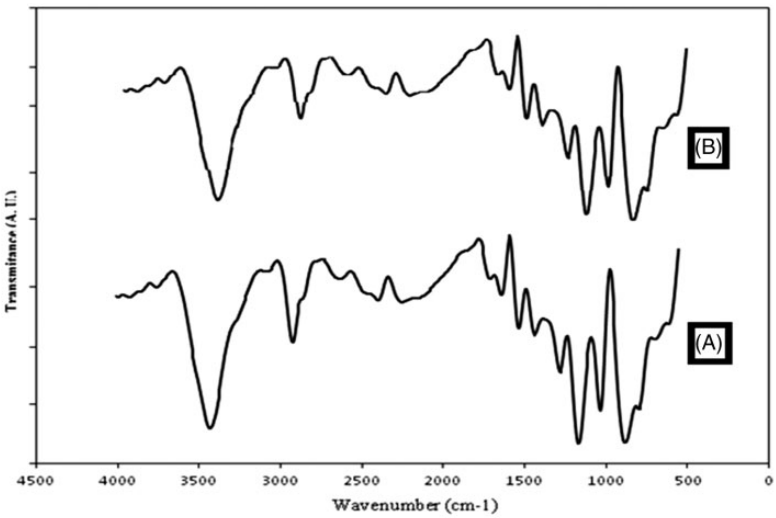

Figure 3. FT-IR spectra of PPy (A) and PPy–ZnO nanocomposite (B).

Design experiment

In this research, the design of the experiment is based on the CCD. Table 2 describes the test design used for qualitative parameters and the evaluation results of the response variables. Statistical analysis of the results was done using Design-Expert software and ANOVA. For this purpose, the effect of two factors on the number of passages of the waste water sample from the filter and the thickness of filtration has been investigated in three levels and the optimal results of the experiment are determined. The obtained responses include optimal quality parameters.

Table 2. Central composite design and results of assessment of response variables.

Run	A: I[a]	B: H[b]	BOD (%)	COD (%)	Hardness (%)	Color (%)	Organic compounds (%)	TDS (%)	pH value increasing (%)	Salinity (%)
1	1	0	99.66	99.65	19.30	54.35	73.00	30.60	65.57	40.00
2	0	0	99.37	99.37	40.35	26.09	67.00	19.62	47.54	50.00
3	0	0	99.30	99.29	40.35	23.91	68.00	19.77	39.34	50.00
4	1	−1	99.28	99.25	10.53	50.00	74.00	27.31	59.84	45.00
5	0	1	99.08	99.09	14.04	30.43	74.00	21.52	47.54	50.00
6	0	−1	99.08	99.10	33.33	54.35	63.00	1.83	35.25	45.00
7	0	0	99.40	99.40	40.35	26.09	67.00	19.62	55.74	45.00
8	−1	0	99.81	99.80	49.12	61.96	61.00	13.76	41.80	40.00
9	1	1	99.28	99.29	24.56	65.22	85.00	37.77	78.69	55.00
10	−1	1	99.32	99.31	49.12	63.04	67.00	9.96	36.07	50.00
11	0	0	99.37	99.37	42.10	27.17	65.00	19.69	47.54	55.00
12	−1	−1	99.32	99.34	43.86	71.74	56.00	16.40	40.16	40.00
13	0	0	99.42	99.42	38.60	27.17	68.00	19.69	47.54	50.00

BOD: biochemical oxygen demand; COD: chemical oxygen demand; TDS: total dissolved solid.
[a]A: I (Iteration of filter).
[b]B: H (Height of filter).

Considering interference effects and concurrent qualitative parameters on the characteristics of the filter, variance analysis and mathematical models were determined (Table 3). Also, using Design-Expert software, the linear model and grade 2 were determined for the appropriate response variables

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i x_i + \sum \sum_{i<j} \beta_{ij} x_i x_j \tag{1}$$

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i x_i + \sum_{i=1}^{K} \beta_{ii} x_i^2 + \sum \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

In these equations x_i and x_j are independent factors, and β_0, β_i, β_{ij} are regression coefficients obtained from the least squares method.

Response surface and selection of optimal conditions for waste water quality

In this research, the relationship between variables and responses obtained by the response surface method was used. Using this method, it is possible to obtain the optimal conditions of the experiment graphically by three-dimensional (3D plot) curves. The response surface curves for waste water quality parameters are shown in Figures 4 to 11. These figures are indicating the response surface curves of the parameters of TDS, BOD, COD, organic compounds, color, salinity, hardness, and pH based on the filter thickness (B: height) and the number of waste water sample passages through the filter (A: iteration). Finally,

Table 3. Mathematical models for expressing the relation between responses and independent variables.

Responses	Regression equation	Coefficient of determination
BOD	Y = 99.36084 – 0.04027*A + 0.474025*A*B	$R^2 = 0.844069$ $R^2_{adjusted} = 0.763249$
COD	Y = 99.36111 – 0.04188*A + 1.67E-05*B + 0.4887*A*B	$R^2 = 0.741887$ $R^2_{adjusted} = 0.660377$
Hardness	Y = 34.278 – 14.7661*A + 3.508775*B	$R^2 = 0.673535$ $R^2_{adjusted} = 0.629017$
Color	Y = 38.70805 – 4.52898*A – 2.89853*B + 1.08695*A*B + 13.18402*A^2 – 0.13118*B^2	$R^2 = 0.669475$ $R^2_{adjusted} = 0.572757$
TDS	Y = 16.44511 + 9.260617*A + 3.95315*B + 2.809288*A*B + 4.240938*A^2 + 3.051338 * B^2	$R^2 = 0.756206$ $R^2_{adjusted} = 0.641479$
pH	Y = 43.19051 + 14.34433*A + 4.508333*B + 5.123125*A*B + 7.377026*A^2 + 6.147526*B^2	$R^2 = 0.784831$ $R^2_{adjusted} = 0.683575$
Salinity	Y = 47.30769 + 1.666667*A + 4.166667*B + 1.25*A*B	$R^2 = 0.892403$ $R^2_{adjusted} = 0.795267$
organic compounds	Y = 66.50928 + 8*A + 5.5*B – 1.375*A*B + 2.198276*A^2 + 1.698276*B^2	$R^2 = 0.957878$ $R^2_{adjusted} = 0.938055$

BOD: biochemical oxygen demand; COD: chemical oxygen demand; TDS: total dissolved solid.

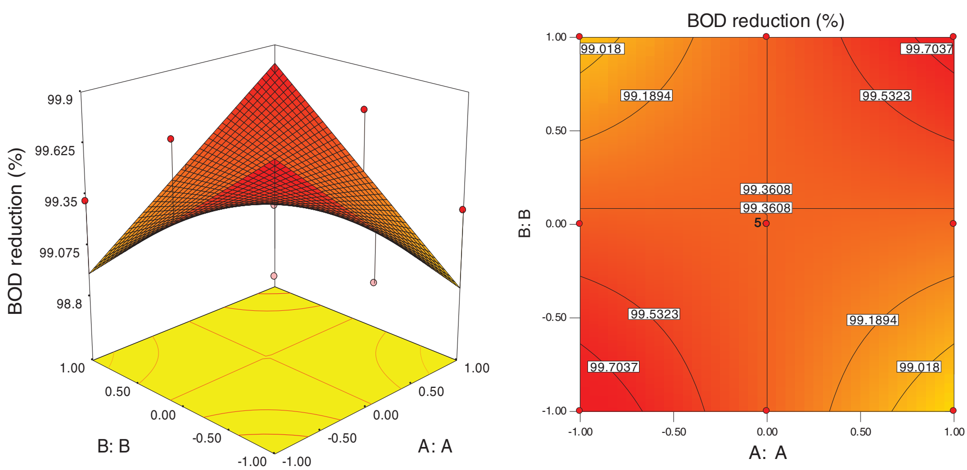

Figure 4. Plots of BOD reduction percentages based on iteration and filter thickness. BOD: biochemical oxygen demand.

Figure 12 simultaneously shows the responses of all considered qualitative variables in relation to the thickness parameters and iteration of filtration.

BOD study. Figure 4 shows that the lowest BOD (the highest BOD decreasing percent) is obtained when the filtration is iterated approximately 8–10 times and the filter thickness

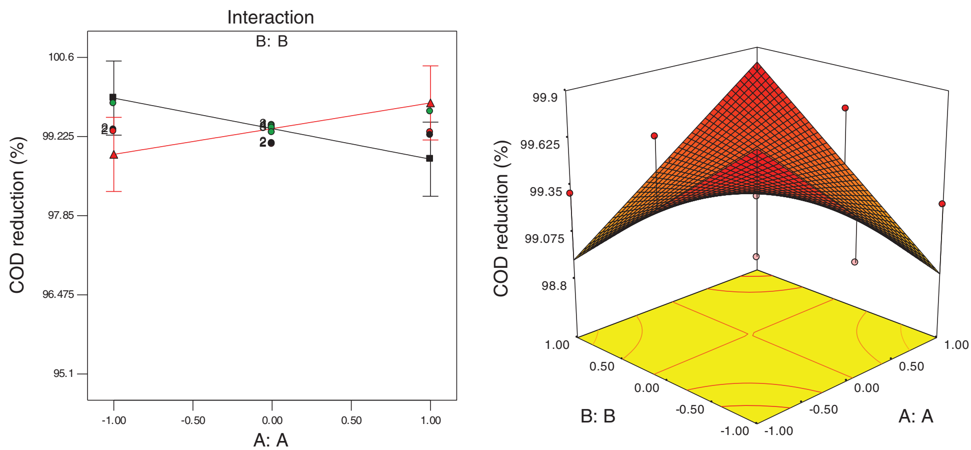

Figure 5. Plots of COD reduction percentage based on iteration and filter thickness. COD: chemical oxygen demand.

is about 4 cm. In the maximum filter thickness condition, BOD decreases with increasing filtration iteration, and in the minimum filter thickness condition, BOD increases with increasing filtration iteration condition. The 3D plot shows that to what extent the height of the filter is low or, in other words, the more the filter is compact (less porosity or permeability), the filter performance to reduce BOD will be less. The higher the filter height or filter porosity, the better filter efficiency to reduce the BOD.

COD study. According to Figure 5, the lowest COD (the highest COD decreasing percent) is obtained when the filtration is iterated approximately 8–10 times and the filter thickness is about 4 cm or the filtration is iterated approximately 1–2 times, and the filtration thickness about 1 cm. Also, the interaction diagram shows that there is no significant difference between the minimum and maximum thickness of the filter in the five times iteration. In the maximum filter thickness condition, COD decreases with increasing filtration iteration, and in the minimum filter thickness condition, COD increases with increasing filtration iteration. The 3D plot shows that to what extent the height of the filter is low or, in other words, the more the filter is compact (less porosity or permeability), the filter performance to reduce COD will be less. The higher the filter height or filter porosity, the better filter efficiency to reduce the COD. In a study by Zhang et al. (2007), a combination of nano-filaments of zinc oxide and titanium oxide as a photocatalyst produced to the vacuum evaporation method and the sol–gel method were used to measure COD. Using this combination has improved the separation of loads and increased spectral range and showed only better performance than titanium oxide. This method has been accompanied by good results for groundwater with low COD values (Zhang et al., 2007).

Hardness study. As shown in Figure 6, the lowest hardness (the highest hardness decreasing percent) is obtained when the filtration is iterated about 2–4 times and the filter thickness is about 1–4 cm. Also, the interaction diagram shows that in total number of filtration iteration, there is no significant difference between the minimum and the maximum filter

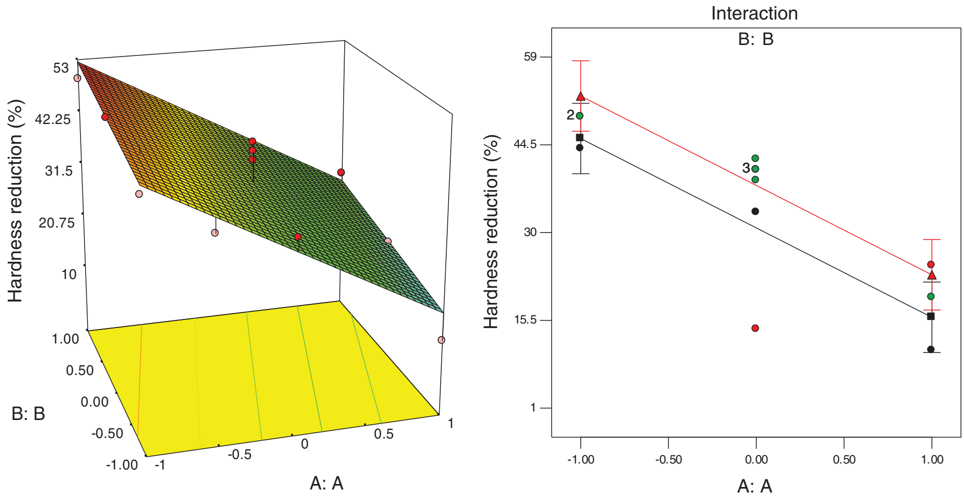

Figure 6. Plots of hardness reduction percentage based on iteration and filter thickness.

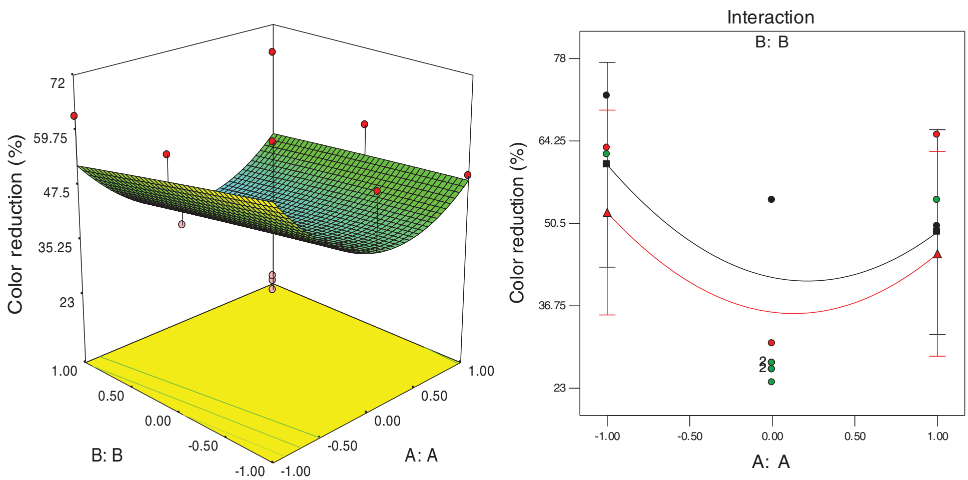

Figure 7. Plots of color reduction percentage based on iteration and filter thickness.

thickness. In the conditions of minimum and maximum filter thickness, with increasing filtration iteration, hardness increases.

Color study. Figure7 shows that the lowest color (the highest color decreasing percent) is obtained when the filtration is iterated about 1–2 times and the filter thickness is about 1–4 cm. Also, the interaction diagram shows that in the minimum filter thickness condition and maximum filter thickness condition with increasing filtration iteration, color increases in lower repeats and gradually decreases in higher iterations. In total number of filtration iteration, there is no significant difference between the minimum and the maximum filter thickness. By increasing the filtration time after two repetitions, it is determined that not

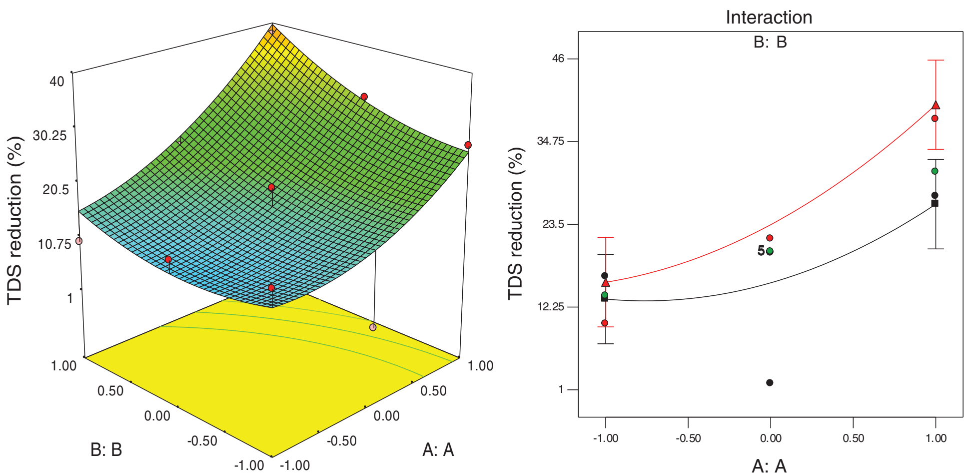

Figure 8. Plots of TDS reduction percentage based on iteration and filter thickness. TDS: total dissolved solid.

only color improvement has not occurred, but also the color quality of the sample has worsened and this can be due to the dissolution of PPy–ZnO particles in the sample, which worsens the sample state.

TDS study. According to Figure 8, the lowest TDS (the highest TDS decreasing percent) is obtained when the filtration is iterated about 8–10 times and the filter thickness is about 3.5–4 cm. Also, the interaction diagram shows that in high iteration filtration there is a greater difference between the minimum and maximum thickness of the filter. In the conditions of minimum and maximum filter thickness, TDS decreases with increasing filtration iteration. The 3D plot shows that to what extent the height of the filter is low or, in other words, the more the filter is compact (less porosity or permeability), the filter performance to reduce TDS will be less. The higher the filter height or filter porosity, the better filter efficiency to reduce the TDS. Therefore, it can be said that the interaction between filter and solid particles was occurred and the filtration process was done in high levels, which improves TDS removal efficiency. Also, by increasing the filtration thickness, the surface of the polymer particles increases with the solids and the amount of adsorption increases.

pH study. Figure 9 shows that the highest pH (the highest pH increasing percent) is obtained when the filtration is iterated about 7–10 times and the filter thickness is about 4 cm. Also, the interaction diagram shows that in high iteration filtration there is a greater difference between the minimum and maximum thickness of the filter. In the conditions of minimum and maximum filter thickness, pH increases with increasing filtration iteration. The 3D plot shows that to what extent the height of the filter is low or, in other words, the more the filter is compact (less porosity or permeability), the filter performance to increase pH will be less. The higher the filter height or filter porosity, the better filter efficiency to increase the pH.

Organic compounds study. As shown in Figure 10, the lowest organic compounds (the highest organic compounds decreasing percent) are obtained when the filtration is iterated about

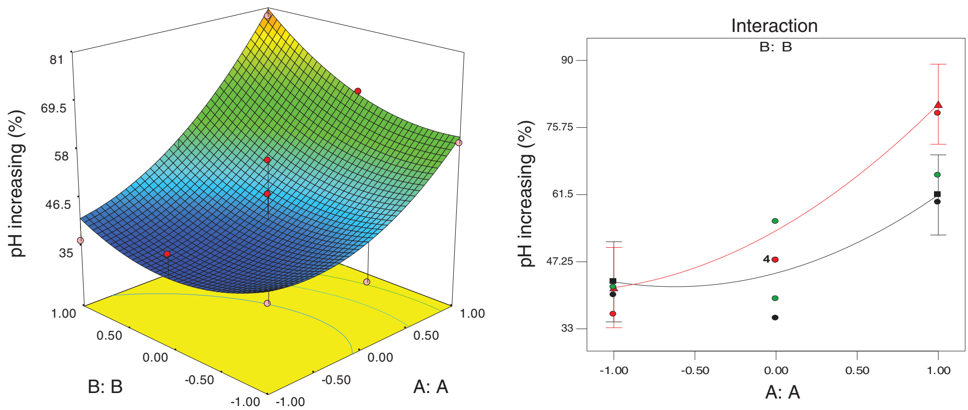

Figure 9. Plots of pH reduction percentage based on iteration and filter thickness.

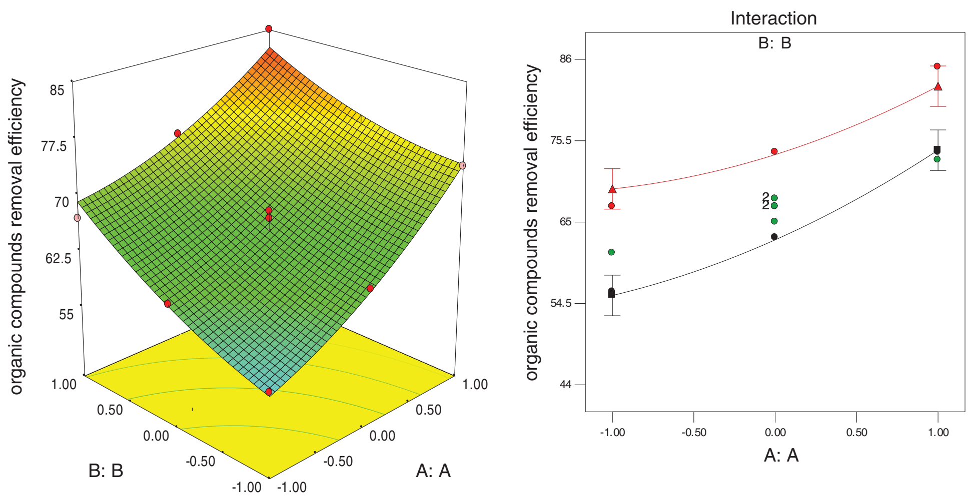

Figure 10. Plots of organic compounds reduction percentages based on iteration and filter thickness.

7–10 times and the filter thickness is about 3.5–4 cm. Also, the interaction diagram shows that in high iteration filtration there is less difference between the minimum and maximum thickness of the filter. In the conditions of minimum and maximum filter thickness, organic compounds decrease with increasing filtration iteration. The 3D plot shows that to what extent the height of the filter is low or, in other words, the more the filter is compact (less porosity or permeability), the filter performance to decrease organic compounds will be less. The higher the filter height or filter porosity, the better filter efficiency to decrease the organic compounds. Whatever the greater the filtration time, the more PPy–ZnO are in contact with the organic compounds, they are more attracted to PPy–ZnO and eventually eliminated more. On the other hand, higher filter height causes more contacts between organic compounds and filter surface so adsorption of organic compounds is done in high level.

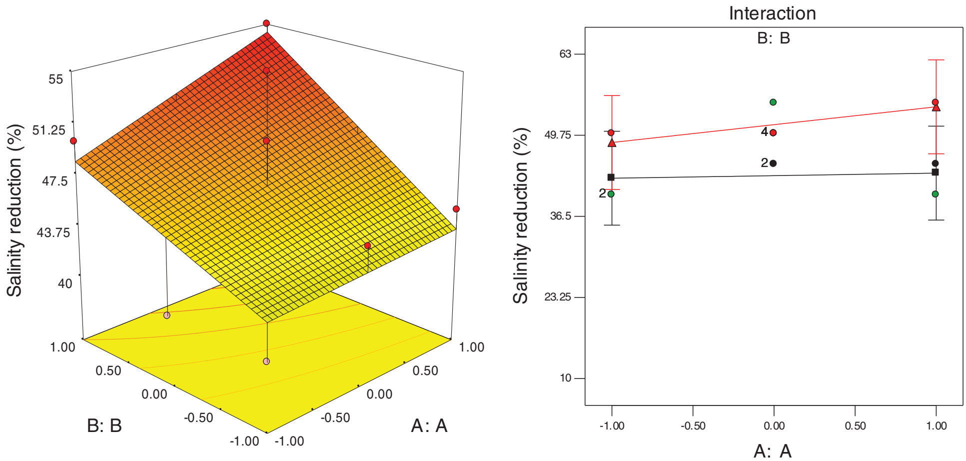

Figure 11. Plots of salinity reduction percentages based on iteration and filter thickness.

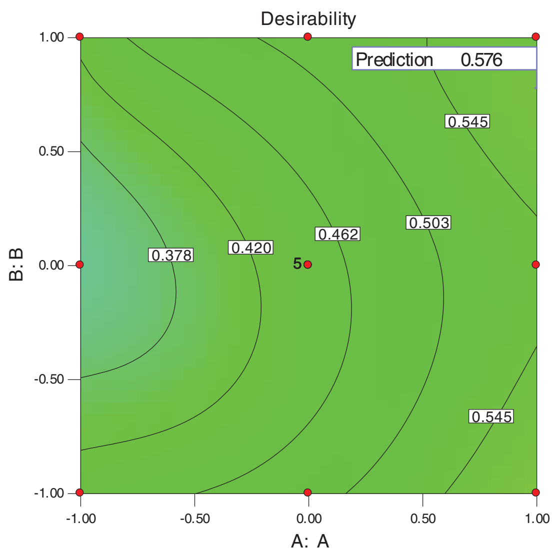

Figure 12. Contour plot of desirability function for obtaining optimal condition.

Salinity study. According to Figure 11, the lowest salinity (the highest salinity decreasing percent) is obtained when the filtration is iterated about 7–10 times and the filter thickness is about 4 cm. Also, the interaction diagram shows that in high iteration filtration there is a greater difference between the minimum and maximum thickness of the filter. In the conditions of minimum and maximum filter thickness, salinity decreases with increasing filtration iteration. The 3D plot shows that to what extent the height of the filter is low or, in other words, the more the filter is compact (less porosity or permeability), the filter performance to decrease salinity will be less.

Table 4. Optimal results using the response surface model.

Variable name	Optimum values	Selected values
Iteration	7–9	8
Height (cm)	3.50–4.00	3.80

In multiobjective optimization, the optimal conditions of a response may not be matched with the optimal conditions of other responses, so both graphical methods and numerical methods are used to find acceptable solutions. In this research, the graphical method (Figure 12) is used to find optimal response. Table 4 shows optimal responses for waste water qualitative variables and independent variables. According to the results obtained, a polyurethane modified with PPy–ZnO has the ability to adsorb organic and mineral compounds and remove them from the water. Therefore, this filter has very good physical and chemical adsorption properties for some pollutants and it has the potential to eliminate or reduce pollutants from wastewater. Therefore, this method can be used to remove pollutants from municipal wastewater.

Conclusion

This project was conducted to optimize waste water quality using modified polyurethane filter with PPy–ZnO nanoparticles. Polymeric filters were provided using a polyurethane surface modification with PPy–ZnO nanoparticles in the form of controlled synthesis by dip coating. The polymerization was carried out in a liquid environment with chloride dopant. After preparing the polyurethane filters, the physical form of the filter was designed and different parameters such as filter sizes were optimized. After designing and optimizing the physical shape and physical parameters, the filter was directly exposed to the water sample at different times and conditions. Sampling from urban waste water was carried out to evaluate the filtering. The morphology and chemical structure of the PPy–ZnO filter were studied by SEM and FT-IR techniques. The results showed that the synthesized polymers were seed like and uniformly synthesized. The best size of synthesized nanoparticles was calculated to be about 50–120 nm. Some waste water parameters including organic compounds, color, hardness, salinity, pH, TDS, BOD, and COD were investigated before and after filtration. The filtration efficiency of designed filter was investigated by spectroscopy and various devices such as BOD and salinity meter. The statistical method of the CCD was used to study the effect of the number of passing waste water samples from filter and filter thickness. The obtained results from mathematical modeling and the response surface method indicated that the optimum filter thickness and optimum filtration iteration were 3.8 cm and eight times, respectively.

Declaration of Conflicting Interests

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