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Effectiveness of Application of TiO2 Nanoparticles in Removing of Heavy Metal Contaminants from Basrah River Water

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***Abstract*— In this study, we focused on the application of Titanium dioxide nanoparticles semiconductor oxides for the removal of heavy metals from Basrah wastewater. Commercial TiO2 was downscaled by ball milling , characterized and tested for heavy metals (Pb, Cd, Hg and Co) removals from the secondary channel of Basrah wastewater (SCBW). Morphology characterization using FT-SEM images indicated that TiO2 particles are of mean grain size 98 nm, Zeta potential measurements revealed the negative charge of the TiO2 particles, X-ray diffraction analysis confirmed anatase phase TiO2 particles , BET measurements exhibited the TiO2 is mesopores with a surface area of 12.65 m2/g , EDX spectrum indicated pure TiO2. The effect of contact time, Temperature, and PH have been taken into account as a parameter to understand the adsorption Mechanism. The best recorded removal percentage was about (97 %) for Pb element after 120 minutes with temperature(T=40o) in Al-Rebat station and reached (100 %) for PH=9. This study has shed light on the importance of TiO2 nanoparticles in removing heavy metals from Basrah river water, which resulted in significant decreases in the concentration of several heavy metals and other pollutants.**

***Keywords*— water treatment, heavy metal removing, Titanium oxide nanoparticles; metal oxides.**Introduction 1.

I. INTRODUCTION

Due to their distinctive characteristics, nanomaterials are currently being used in a variety of real-world applications across a broad spectrum of industries, including the ecosystem, building and transportation sectors, energy storage, electronics, medical, cosmetics, and more. Since the nanomaterials have at least one dimension on the nanoscale scale, their tiny size and high specific surface area provide them outstanding characteristics when compared to bulk phases. Reducing solids to nanoscale particle size reveals new physical properties [1,2]. Different nanoparticle shapes also lead to significant differences in material properties compared to larger sized nanoparticles. Because shape, size, morphology, and other factors can dramatically change the way a material interacts with heavy metal contaminants and other substances, a material's function and properties ultimately depend on its size, shape, and surface roughness [3]. Nanomaterials have been instrumental in the field of water purification, providing novel avenues for the development of selective and permeable membranes and adsorbents. These characteristics are crucial, especially in light of the finite amount of energy resources that are. A number of current studies that address water treatment using nanomaterial-based technologies are presented. Advanced technologies have utilized nanomaterials consisting of polymers, composites, ceramics, and carbon, among others, and have been shaped into different forms and dimensionalities, including particles (0D), fibers (1D), and films (2D–3D). The main topics of discussion are nanostructured membranes and adsorbents as well as photocatalytic nanosystems that can actively photodecompose organic pollutants like dyes [4,5]. Though most people associate heavy metals with toxicity to living things, lightweight metals like beryllium and lithium can also be harmful [6]. Titanium and are example of metallic oxide semiconductor that can be used to efficiently remove heavy metal contamination from water. Using the bottom-up co-precipitation method, synthetic clay is easily prepared and can be decorated with oxides such as zinc and titanium oxides. The materials produced can be utilized to purify water contaminated with heavy metals [7,8]. The capacity to remove various ion types simultaneously, long retention times, and adsorbent cycling stability are the main challenges facing adsorption techniques. The large-volume sludge formation and post-treatment requirements are crucial problems that must be resolved for chemical techniques, even though the membrane and chemical methods are feasible. Further advancements in membrane separation may result from fouling and scaling inhibition. Pre-treatment and routine membrane cleaning, however, come at an extra expense [9,10,11].

II. EXPERIMENTAL ASPECTS

The physics department at the University of Basrah's College of Science developed the tool used in this work to grind various powders. After making some changes to the device's construction and design, they were able to achieve excellent results when it came to downscaling particle size

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at various milling times. Merck provided 99.7% of the commercially available synthetic titanium dioxide powders, which had an average grain size of roughly 300 nm. Wet grinding was selected for this study over dry grinding for a number of reasons, including: Dry grinding uses more energy than wet grinding, creates larger particles, has a rougher surface, and produces wider particle sizes [12]. More details of the preparation and methods in results and discussions.

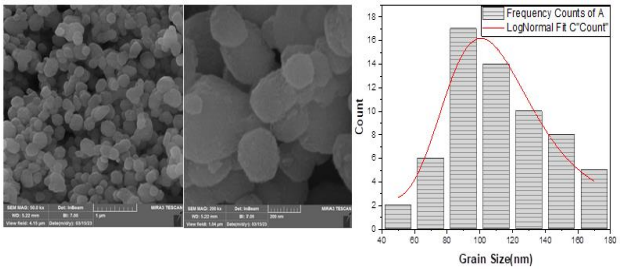

Figure 1: (left panel) two different scales FE-SEM images, and grain size distribution histogram of of TiO2 nanoparticles sample.

Table 1: Grain size statistical parameters according to FE-SEM images and calculations of grain size distribution histogram of of TiO2 nanoparticles sample.

Sample	Mean (nm)	Standard deviation	Minimum (nm)	Median (nm)	Maximum (nm)
TiO2	98.24	31.22	49	102.5	172

III. Results and Discussions

A. Characterization of TiO2 nanoparticles

1) Morphology

Using SEM images of ground TiO2 powder with 10 minutes milling times, the sample surfaces were examined to assess the shape and characterize the surface of the TiO2 particles. Examining the impact of short milling time on the shape and size distribution of TiO2 nanoparticles is the goal of the measurement methodology. Figure 1 displays the SEM micrograph after milling processes, together with particle size distribution histograms of TiO2 nanoparticles. Using the image analysis tool Image-J, we were able to estimate a large number of particle sizes from the exhibited micrographs and collect the size distribution histograms that go along with each image in order to achieve an appropriate statistical interpretation of the data. These results demonstrate the effectiveness of the method and device. Table displays the statistical mean of the TiO2 particle size of ten minutes of milling time. The diameter of the particles ranges between approximately 49 and 172 nm for the material obtained after ten minutes of milling. Table 1 provides a summary of calculations on particle size distributions. It is worth to note that from a closer look at the SEM micrographs that the particles are agglomerated due to the humidity or surface adherence.

2) Energy dispersive X-ray analysis (EDX) for TiO2

The titanium and oxygen characteristic peaks in Figure 3 indicate the sample's purity, and the weight ratio agrees with the theoretical ratio. The findings made it abundantly evident that the sample's titanium content was 56.13% and its oxygen content was 43.87%. This indicates that the TiO2 was completely uncontaminated prior to treating the contaminated water.

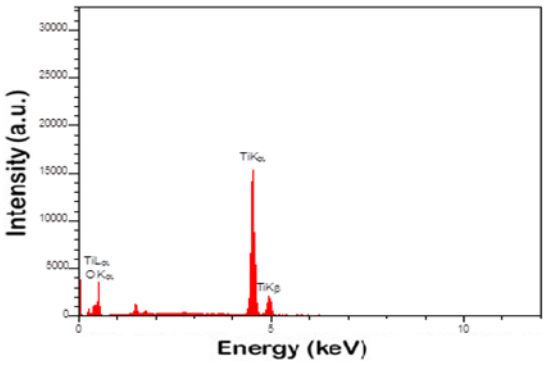

Figure 2: EDX (Energy-dispersive X-ray spectroscopy) spectra of TiO2 sample

3) X-ray diffraction analysis for TiO2

The XRD pattern in Fig 3 showed many characteristic bands at the 2θ position (27.68°, 36.31°, 39.41°, 41.47°, 44.27°, 54.54° and 69.17°) and had FWHM values (0.1968, 0.2952, 0.2460, 0.1968,0.2460, 0.2952 and 0.4428 2θ, respectively). These results correspond with previous studies [13], which confirm the prepared titanium oxide compound. The average crystal size was calculated using the Debye-Sherrer equation and gave a value of 30.16 nm. The X-ray diffraction pattern is shown in Figure 3.

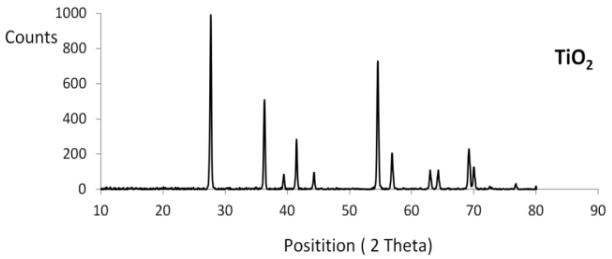

Figure 3. X-ray diffraction (XRD) correspond to the ball milled TiO2 anatase phase.

4) 3.1.4 Determination of Zeta potential for TiO2

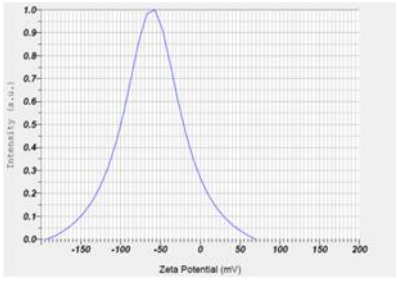

Figure 4: Zeta potential analysis of ball milled downscaled TiO2 nanoparticles.

The zeta potential analysis of titanium oxide appeared more stable in their aqueous solution and also it has a negative charge onto the outer surface. The data of zeta potential was recorded at -57 mV and shown in Figure 4.

5) Surface area and porosity analyses (BET)

The functional groups and pore structures on an adsorbent surface essentially determine its adsorption efficiency [14]. However, there are three different kinds of structural pores: macropores, mesopores, and micropores [15]. Many techniques, including Barrett Joyner Halenda (BJH), Brunauer Emmett Teller (BET), T-Plot, and Langmuir, are used to determine a material's surface value. These techniques involve the occupation of all active sites on the material's outer surface by inert gases, such as nitrogen, and a temperature of 77 K, at which the molecules of the inert gas are formed. The quantity of these desorption molecules indicates the surface value of the material [12]. The titanium surface area and pore structure type were computed using the BET and BJH techniques. The mesoporous structure and surface area of 12.65 m2/g were revealed by the results.

Simulation of effluents

Three effluent samples were collected from some inner rivers (Al-Khora, Al-Ashar, and Al-Rebate stations) of Shatt al-Arab River (located in downtown Basrah Governorate in southern Iraq) at a depth of 15 cm from the water surface using a special water sample instrument (jar) in the winter season (December 2022).

The as-collected samples were found to have some physicochemical properties using a multimeter (WTW Multi 3210, Germany). They were then placed in a polyethylene container and kept cool. Afterwards, the effluent samples were transported to the laboratory for separate experiments to remove any suspended materials. The resulting samples were contaminated using 10 mg/l of the standard solution of some elements such as zinc, lead, copper, and cadmium. achieve the optimal conditions for the removal of these elements such as the contact time, temperature and acid a special function, adsorption processes were performed by shaking the samples in an incubator (Certomat IS, Germany). All measurements were obtained using ICP-OES instrument (Thermo Fisher Scientific).

B. Removal of some heavy metals by TiO2

1) Effect of contact time

The contact time following the removal of four heavy metals from the TiO2 surface showed that zinc ions in the Al-Rebat station had the highest removal efficiency at 15 minutes and 78.04% compared to the other ions. At the same contact time of 30 minutes, the adsorption percent for zinc ions was recorded in the Al-Kkhora and Al-Ashar stations. Al-Arebat station recorded the shortest contact time and highest removal percent at 15 minutes and 96.7%. The outcomes of eliminating lead ions from their aqueous solution matched those of eliminating zinc ions. When compared to the other ions adsorbed onto the titanium oxide surface, the data of the contact time effect for removing cadmium ions showed a low adsorption percentage in all stations. Conversely, the Al-Khora station demonstrated a higher percentage of cadmium ion removal than the other contaminated stations. The Al-Rebat station produced the highest removal % results for copper ions on titanium oxide, which were identical to the removal results for zinc and lead. This could be because Al-Rebat had a lower salt composition than the other stations, which reduced competition between the salts containing zinc, lead, and copper ions. Table 2 lists all of the findings regarding the impact of contact time on adsorption efficiency for the removal of Zn2+, Pb2+, Cd2+ and Cu2+ from the surface of titanium oxide nanoparticles.

Table 2: Effect of contact time for Removal of some heavy metals onto TiO2

	Contact time (min)	Zinc	Lead	Cadmium	Copper
		C_e ppm (%R)	C_e ppm (%R)	C_e ppm (%R)	C_e ppm (%R)
Al-Khora	5	2.9050 (70.94)	1.7037 (82.96)	9.4165 (5.83)	5.5792 (44.20)
	15	2.5012 (74.98)	1.3475 (86.52)	8.3912 (16.08)	5.1616 (48.38)
	30	2.2506 (77.49)	1.3424 (86.57)	7.1450 (28.55)	4.3763 (56.23)
	60	2.1142 (78.85)	1.1442 (88.55)	7.0677 (29.32)	4.2791 (57.20)
	120	2.0049 (79.95)	1.0361 (89.63)	6.7508 (32.49)	4.0997 (59)
Al-Ashar	5	2.9793 (70.20)	2.9242 (70.75)	9.7117 (2.88)	5.1044 (48.95)
	15	2.5154 (74.84)	2.2032 (77.96)	8.5722 (14.27)	4.2047 (57.95)
	30	2.2224 (77.77)	1.9826 (80.17)	8.3557 (16.44)	3.7845 (62.15)
	60	2.2169 (77.83)	1.8617 (81.38)	8.2947 (17.05)	3.5691 (64.30)
	120	2.1407 (78.59)	1.8244 (81.75)	8.0932 (19.06)	3.4223 (65.77)
Al-Rebat	5	2.9266 (70.73)	1.3810 (86.19)	9.5038 (4.96)	5.1791 (48.20)
	15	2.1956 (78.04)	0.3295 (96.70)	9.1357 (8.64)	4.8842 (51.15)
	30	2.1557 (78.44)	0.3128 (96.87)	8.9368 (10.63)	4.2723 (57.27)
	60	2.0759 (79.24)	0.2299 (97.70)	8.7965 (12.03)	3.6736 (63.26)
	120	1.9569 (80.43)	0.2233 (97.76)	8.6945 (13.05)	3.5031 (64.96)

2) Effect of temperature

When the other parameters are fixed, the removal percentage of zinc ions from titanium oxide has been recorded at a high value, falling between 92.9 and 94.2%. Because of the weak bond between titanium oxide and zinc ions, the highest removal percent is found in Al-Rebat polluted water at the lowest temperature. This is because the zeta potential analysis indicates that a higher surface negative charge corresponds to a higher positive charge for zinc ions. Generally speaking, a difference in charges between the adsorbent and the adsorbate increases the removal percentage. [16]. The following was the order for stations' removal percent. Al-Ashar > Al-Khora > Al-Rebat. Al-Ashar station recorded a lower removal percent than the other stations, while AlRebat polluted water showed the highest removal percent of lead ions onto titanium oxide surface at 40 ºC and exhibited similar behavior at 30 ºC. Additionally, raise the percentage of removal ascribed to particle size, surface shape, and surface charge [17]. At 30 ºC, Al-khora station recorded the lowest removal percent of cadmium ions onto titanium oxide surface, whereas Al-Ashar and Al-Rebate were reported to have the highest removal percents, at 58.6 and 53.83, respectively. In every station, copper ions had a higher removal percentage on

titanium oxide surfaces than cadmium ions. Owing to the fact that copper ions are smaller in size than cadmium ions [18], Al-Ashar and Al-khora polluted water typically had the highest removal percentages at 30 ºC (87.06 and 86.77%, respectively), while Al-Rebat station recorded 85.98% at 20 ºC. Table 3 contains a list of all the findings of the removal percentage for copper, zinc, lead, and cadmium ions onto TiO2 nanoparticles.

Table 3: Effect of temperature for Removal of some heavy metals onto TiO2

Station	Temperature (ºC)	Zinc	Lead	Cadmium	Copper
		C_e ppm (%R)	C_e ppm (%R)	C_e ppm (%R)	C_e ppm (%R)
Al-Khora	20	0.92441 (90.75)	0.35587 (96.44)	6.158031 (38.41)	1.66185 (83.38)
	30	0.70943 (92.90)	0.290823 (97.09)	5.157355 (48.42)	1.322476 (86.77)
	40	0.79826 (92.01)	0.37071 (96.29)	5.759481 (42.40)	1.582792 (84.17)
	50	0.88953 (91.10)	0.56281 (94.37)	6.278879 (37.21)	2.05417 (79.45)
Al-Ashar	20	0.72779 (92.72)	1.05982 (89.40)	4.139279 (58.60)	1.37243 (86.27)
	30	0.65255 (93.47)	0.99928 (90)	4.486738 (55.13)	1.29399 (87.06)
	40	0.80737 (91.92)	0.88685 (91.13)	4.94632 (50.53)	1.33237 (86.67)
	50	0.837922 (91.62)	1.239563 (87.60)	5.390186 (46.09)	1.709961 (82.90)
Al-Rebat	20	0.578952 (94.21)	0.204105 (97.95)	4.617541 (53.82)	1.401157 (85.98)
	30	0.614572 (93.85)	0.213568 (97.86)	4.974939 (50.25)	1.553107 (84.46)
	40	0.774448 (92.25)	0.200601 (97.99)	5.946713 (40.53)	1.478156 (85.21)
	50	0.936849 (90.63)	0.293101 (97.06)	6.648309 (33.51)	2.417042 (75.82)

3) Effect of the pH level

In all stations, the data pertaining to the removal of zinc ions from the titanium oxide surface showed a convergence of the removal value at pH 3 and 6. At pH 9, the removal percentage clearly increased, possibly as a result of the adsorption surface's increased negative charge. The adsorption percentage increased as the concentration of hydrogen ions decreased, which may be because of a decrease in their competition. Lead ions also seemed to have a low removal efficiency onto titanium oxide with increasing acidity levels. The removal efficiency of cadmium ions from titanium oxide surfaces was positively correlated with pH level changes more so than with other factors. The highest removal percentage, 79.08%, was recorded in the Al-Rebat station at pH 9, where it was linked to a decrease in the concentration of hydrogen ions [19,20]. This is explained by an increase in the attraction between cadmium ions and titanium oxide surface. With an increasing negative charge towards the basic medium, the removal percentage of copper ions was progressively increased on the titanium surface. At pH 9, the Al-Rebat station recorded the highest removal percentage of 99.11%. Table 4 presents a comprehensive list of the removal percentages for zinc, lead, cadmium, and copper ions onto TiO2 nanoparticles.

Table 4: Effect of the pH level for Removal of some heavy metals onto TiO2

Station	pH	Zinc	Lead	Cadmium	Copper
		C_e ppm (%R)	C_e ppm (%R)	C_e ppm (%R)	C_e ppm (%R)
Al-Khora	3	1.75869 (82.41)	5.32247 (46.77)	2.37214 (76.27)	5.86708 (41.32)
	6	1.662805 (83.37)	0.24104 (97.58)	2.37214 (76.27)	3.76212 (62.37)
	9	0 (100)	0 (100)	2.259735 (77.40)	0.11694 (98.83)
Al-Ashar	3	1.822613 (81.77)	6.16938 (38.30)	2.360096 (76.39)	5.92413 (40.75)
	6	1.610867 (83.89)	0.30618 (96.93)	2.348053 (76.51)	0.96691 (90.33)
	9	0.212545 (97.87)	0 (100)	2.323966 (76.76)	0.43069 (95.69)
Al-Rebat	3	1.742709 (82.57)	5.550489 (44.49)	2.376154 (76.23)	6.043925 (39.56)
	6	1.578905 (84.21)	0.20846 (97.91)	2.368125 (76.31)	2.38163 (76.18)
	9	0 (100)	0 (100)	2.091128 (79.08)	0.08842 (99.11)

IV. Conclusions

In brief, the ball milling process was effective in downscaling TiO2 nanoparticles for use in heavy metal removal applications involving Basrah river water. Various characterization techniques were employed to investigate the TiO2 nanoparticles' size, shape, volume, porosity, and charge. To comprehend the adsorption process, the effects of temperature, PH, and contact time have been considered. When effectively removed Zn2+, Pb2+, Cd2+, and Cu2+ from the surface of titanium oxide nanoparticles at a PH level equal to 9, this multifunctional TiO2 nanomaterial produced the highest removal rates of heavy metals.

Conflict of interest

Authors declare that they have no conflict of interest

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