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Evaluation of Water Treatment Residue as a Sorption Medium and its Application to Control Phosphate Level in Water

Abstract- Wastewater treatment residual material, WTR, from a local drinking water facility in Baghdad, was evaluated as a potential medium for the removal of some unwanted species from water. The material was first characterized by chemical composition, X-ray diffraction and infrared spectral analysis prior to its use as an adsorbent. The x-ray revealed that the material is a calcium based water treatment residue mixed with silica and impurities of oxides like MgO and Fe₂O₃. The adsorption characteristics of the material were evaluated by studying the adsorption of methylene blue. The cation exchange capacity and the surface area had values of 10.5 mmol per 100 g and 87.5 m².g⁻¹, respectively. The sorption capacity of the material was applied to control the phosphate concentration in water. Time and adsorbent amount have played significant roles in the removal of phosphate from water. An adsorption capacity had a value of 1.6 mg PO₄³⁻.g⁻¹ of WTR.

Keywords- Kaolin-polyacrylamide composite, Nickel adsorption, experimental design; optimization, adsorption (efficiency and capacity)

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1. Introduction

There exists a growing interest in the search for low cost and reliable adsorbents for the removal of pollutants from water. Various materials were suggested and used on lab and pilot scales as potential sorbents such as residual chars from plant materials, clay minerals, fly ashes, etc. De Gisi et al. [1] have reviewed the characteristics and adsorption capacities of so many sorbents for wastewater treatment to remove organic and inorganic pollutants. The introduction of a new adsorbent for use in environmental applications must be aided by procedures for the evaluation of sorption characteristics using methylene blue, MB, dye from aqueous solutions [2]. The MB method yields accurate prediction of some sorbent index properties and can be easily applied with simple test equipment [2].

Lee et al. have studied the use of aluminum-based WTR for the phosphate adsorption to examine the effect of pH, range of particle size in addition to temperature [3]. The increase of WTR particle sizes caused a decrease in adsorption rate. The use of fine WTR particles at pH 4 resulted in the highest P adsorption capacity, 15.57 mg PO₄⁻ /g WTR. Higher pH ranges (7-9) has required much longer sorption time. Zhou and Haynes, 2010, reviewed the effect of working parameters on the sorption efficiency of heavy metal ions on WTR

[4]. Sarkar et al. [5] evaluated the sorption of two As species by Fe- and Al-based WTR as affected by the particle size at different pH values. Both WTRs showed high affinity for As oxyanions. Suda et al. [6] used WTR to stabilize arsenic in flooded soils and attenuate arsenic uptake by rice (*Oryza sativa*L.) plants. Drinking Water Treatment Residual was characterized by Zhao et al. [7] as a novel pesticides adsorbent. The WTRs exhibited a greater affinity for chlorpyrifos accompanied by a high sorption capacity (KF = 5967 mg1-n.L.Kg-1 due to the type and content of organic matter. Park et al. [8] studied the utilization of WTR as substitute soil to enhance plant growth. A cost-effective remediation method could be established by the in situ application of Ca-WTR for soils the contaminated with Cu without affecting citrus production [9]. The use of dewatering WTR will alter its ability to decrease the P soil concentrations. It also affects the metal concentrations [10].

Eutrophication processes pose a serious threat for the surface water bodies. Phosphate represents a major cause of eutrophication and excess of biogenic substances coming from drainage areas deteriorates the quality values of natural waters, and results in changes in the structure of water body ecosystems. They triggers vigorous growth of cyanobacteria, reduces dissolved oxygen

content, and consequently suffocates fish populations. The process will complicate water purification. There must be means for the minimization of biogenic discharge of nitrogen and phosphorus compounds into the water bodies. The removal of phosphate from the wastewater is another mean for the control of these species from water. Ruzhitskaya and Gogina [11] have summarized the methods of phosphate removal from wastewater. Chang-jun, et al. used active red mud and a waste of alumina industry, for the adsorption of phosphate from water. The adsorption process followed well the Langmuir isotherm model with maximum adsorption capacities of the acid-heat activated red mud and the heat activated samples of 202.9 mg P/g and 155.2 mg P/g, respectively [12]. Barbooti, has used magnesium oxide for the control of phosphate in water originating from the application of cattle manure for soil amendment [13]. Recently, Goscianska, et al., succeeded to remove phosphate from water by lanthanum-modified zeolites derived from fly ash. The sorption capacities of the particular samples were in the range of 44.0 – 58.2 mg.g-1 [14]. Recently, Wang et al., examined the activity of WTR as an additional medium in columns for effective P removal from eutrophic surface water .

The present work is an attempt to evaluate the potentials of WTR from a local drinking water facility as a sorbent by methylene blue adsorption and its application for phosphate removal from aqueous solutions.

2. Materials and methods

I. Apparatus

The concentration of phosphate and methylene blue was measured by spectral absorption on a EMC Lab, GMBH, Germany, (UV-1100) spectrophotometer. The infrared spectra were recorded on a Fourier Transform infrared, FTIR, spectrometer from Shimadzu (8300) on KBr discs. The X-ray diffraction, XRD, measurements were recorded on a diffractometer from FEI Co., F350 NE Dawson Creek Drive Hillsboro, 9712, USA. The sorption experiments involved the shaking of the samples with Genex, shaker, Florida, USA.

II. Materials and reagents

The phosphate standard solution was prepared from potassium dihydrogen phosphate supplied from BDH. The MB and ammonium *p*-molybdate were supplied from Reidel de Haene, Germany; The WTR was obtained from a local drinking water facility in Baghdad. It was naturally dried

and ground in an agate mortar to pass 0.06 mm mesh.

III. Procedures

The CEC determination: A known amount (2.00 g) of the material was mixed with distilled water (300 mL) in a beaker. Sufficient sulfuric acid was also added with stirring to acidify the solution to a pH range of 2.5 to 3.8. The methylene blue solution (0.01 M) was placed in a burette. Aliquot of 5 mL of the solution was added to the slurry and the mixture was stirred for 1 to 2 min. A drop of the water-WTR suspension was placed near the circumstance of a filter paper. One mL increments of the methylene blue solution were added to the slurry with 1 to 2 min of stirring after each addition, followed by transferring a drop onto on the filter paper [16]. To indicate the end point a light blue halo around the drop forms [17].

Surface area determination: The specific surface area can also be determined from the MB adsorption results by Santarina et al., [18]. From the area covered by one methylene blue molecule is typically was assumed to be 130 Å² (1 Å = 0.1 nm) the overall surface area of the sorbent was measured. It is important to highlight that the technique is done in water suspensions. Thus expansive minerals can expose all available surface area [19]. The value of the specific surface was derived from the point of complete cation replacement determined on the titration curve. The step-by-step procedure was given as follows:

- Accurately about 2.0 g of the dry specimen was mixed with 200 mL of deionized water;
- The MB solution was added to the soil suspension and continually mixed for about 2 h, The mixture was then left overnight to reach absorption equilibrium and allow particle settlement;
- Five mLs aliquot of the fluid was carefully removed and placed in a test tube and centrifuged;
- The remnant concentration of MB in the fluid was measured (spectrophotometer, wavelength = 666 nm, was used); More MB solution was added and the previous steps were repeated (for convenience, a set of suspensions can be prepared in advance);

Adsorption study: In 60 – mL capacity plastic containers, weighed amounts of the WTR (0.05, 0.10, 0.15 and 0.220 g) were placed and fixed amount of MB solution (2mL) was added. The

volume was completed up to 50 mL with deionized water. The container was capped and further wrapped with Parafilm. The containers were placed on the top of the rotary shaker and shaken at 250 rpm. The containers were removed from the shaker at various time intervals (22, 35 and 60 min.), centrifuged and filtered with syringe filters with a pore size of 0.2 μ . The filtrates were analyzed by spectral absorption.

Phosphate removal experiments: In a set of seven containers, aliquots of phosphate solution that makes 50 mg.L⁻¹ when diluted to the final volume (50 mL) were placed, a fixed amount of WTR (0.4 g) was added. No adjustment of pH was made, nor any KCl was added to mimic normal wastewater environment. The containers were placed on the top of the rotary shaker operating at 250 rpm to be removed after a predetermined time of equilibration. The samples were filtered with a microsyringe (0.2 μ) and the filtrate was kept at 4° C until the analysis time. The sample solutions together with standard phosphate solutions were analyzed on the same day to insure similarity in analytical conditions. To study the sorption activity of WTR towards MB, a method was first established for the rapid analysis of samples after the sorption. The MB concentration was determined by the spectrophotometric method by measuring the absorbance of the solutions at 666 nm.

3. Results and Discussion

1. The WTR characterization

The material was characterized by chemical analysis and found to be composed mainly of lime (or limestone), in addition to organic matter and other minor oxides (Table 1). Some of the calcium exists as other species like calcium silicate. To confirm the composition, the material was ignited at 800 °C to remove the organic material and decarboxylate limestone that may be present. Figure 1 shows the x-ray diffraction patterns of the WTR and its residue after burning at 800° C. On ignition; the Calcium content was almost doubled accompanied by reduction of the carbon content by about 40%. The low aluminum and iron content reflects the relatively small amounts of the alums and hence, low suspended matter in the treated water [21]. Such a composition is indicative of the differences in the composition of the local WTR in comparison with those employed in the published papers.

Table 1: The chemical composition of the wastewater treatment residue

Element, %	Sample	
	Dried WTR	Fired WTR
Ca	16.65	37.37
C	9.46	5.13
Si	8.51	5.68
Mg	4.15	1.57
Fe	2.81	2.38
Al	2.63	2.81
O	54.49	44.81

Figure 2 shows the FTIR spectra of the dried WTR together with that burned at 850° C. The spectrum of the dried material showed the main features being, 1420, 874 and 710 cm^{-1} of the IR bands of calcium carbonate [21,22]. Also, the C-H signals appeared in the 2900 – 3300 cm^{-1}) referring to some organic contaminants. The wide and strong band within the 500 cm^{-1} regions can be attributed to the Ca-O bond [23]. The main features of the spectrum vanished after burning of the WTR at 850° C indicating the degradation of the organic compounds and thermal decomposition of calcium carbonate. Only the features of the inorganic oxide residues persisted below the 1000 cm^{-1} .

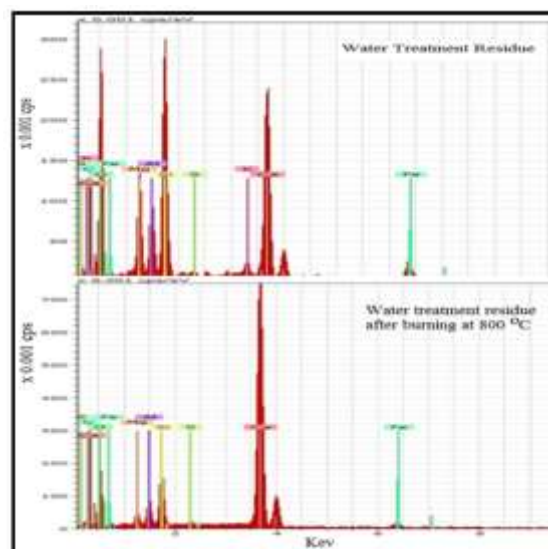


Figure 1: The x-ray diffraction patterns of the water treatment residue (upper) and after burning at 800° C (Lower).

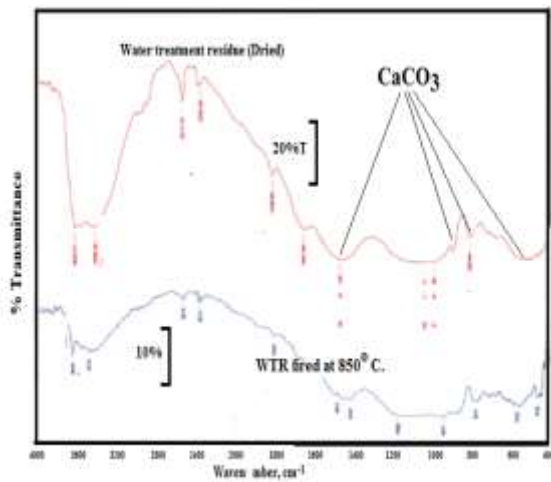


Figure 2 FTIR spectra of the dried WTR and that burned at 850° C.

II. Sorption activity

The method is sensitive and indicated a linear calibration graph (Figure 3) with R² of 0.997 and absorbance concentration relation as given in Equation 1:

$$\text{Abs} = 60.59 \text{ C(M)} + 0.0596 \quad (1)$$

The determination of CEC was carried out based on the Standard Test Method for MB Index of Clay, (ASTM C 837 -81) [25]. The test was based on the linear relationship between the MB index and fundamental properties of the sorbent such as cation exchange capacity (CEC) and specific surface. The CEC could then be calculated as in equation (2):

$$\text{CEC} = (\text{EV} / \text{W}) * 100 \quad (2)$$

The CEC refers to the cation exchange capacity in meq/ 100 g of the WTR sample. The E was the number of MB milliequivalents per /mL. V is the volume of MB solution required for the titration, and W was the weight in grams of the dry material.

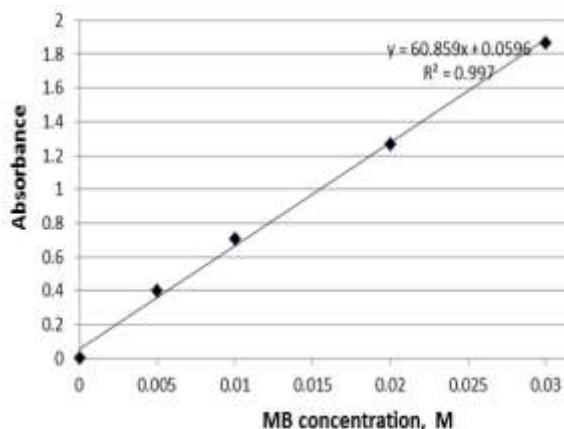


Figure 3: Methylene blue calibration spectrophotometric graph.

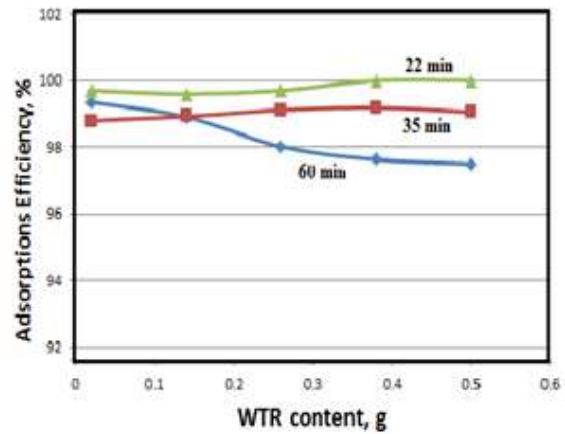


Figure 4: The adsorption profiles of methylene blue on the WTR.

The CEC of WTR evaluated by this method was found to be 10.5 mmol/100 g. The CEC value was more than that of normal clay minerals [26] and much less than the modified clays [17].

For the surface area determination, a plot of the amount of MB added versus the amount of absorbed MB was constructed. The point of complete cation replacement was identified. The specific surface can then be calculated from the amount of MB absorbed at the optimum point:

$$S_s = \frac{m_{MB}}{319.87} A_v A_{MB} \frac{1}{m_s} \quad (3)$$

where m_{MB} was the mass of the absorbed MB at the point of complete cation replacement, and m_s is the mass of the soil specimen, A_v was Avogadro’s number (6.02 × 10²³/ mol), and A_{MB} was the area covered by one MB molecule (typically assumed to be 130 Å²).

The surface area of the material was estimated using the above relation (Eq. 3) and found to be 87.5 m².g⁻¹.

III. Application for PO₄ level control

The phosphomolybdic acid method was employed for the determination of phosphate in water [18]. The standard solution was prepared in the range of 1-10 mh.L⁻¹ and used to prepare the calibration graph. The absorption was measured at 660 nm. The method was linear over the concentration range 0-10 mg.L⁻¹ (Figure 5). The correlation coefficient was 0.982 and the absorbance was related to the concentration by equation 4.

$$\text{Abs}_{660 \text{ nm}} = 0.0629 \text{ C (mg.L}^{-1}\text{)} + 0.136 \quad (4)$$

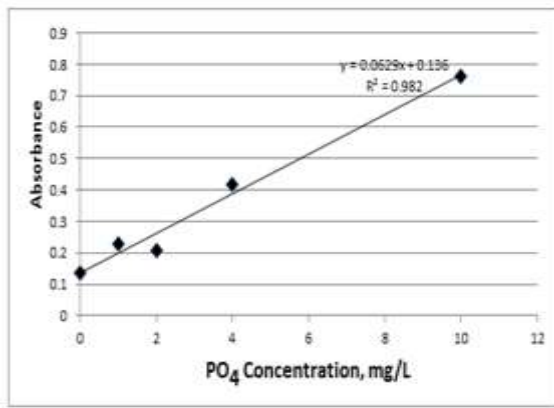


Figure 5: Phosphate spectrophotometric calibration graph.

In contact with WTR, the phosphate content underwent a significant decrease with time. Within 4 h, there was 75% of the phosphate was removed from the water. Thus, about Ca-based WTR for soil amendment will participate in the control of phosphate level in the irrigation water by raising the soil pH and soil available Ca [9]. This allows safe disposal of water to the environment that no further implications may be expected. Quantitatively, 50 ml of 50 mg.L⁻¹ (i.e. 2.5 mg of phosphate) will degrade down to 0.625 mg within 4 h. Capacity wise will assume 1.6 mg PO₄³⁻/g of WTR. The time duration selection was based on the time required for the water to flood the soil and move downward. Gersten, [27] reported that the most significant factors affecting P removal rate with WTR were the particle size. He reported a total P; TP, removal efficiency varied between 58-95%. The increase in particle size from ~ 0.6-2 to 6-20 mm reduced the phosphate adsorption capacity by 30% on average within 6 h.

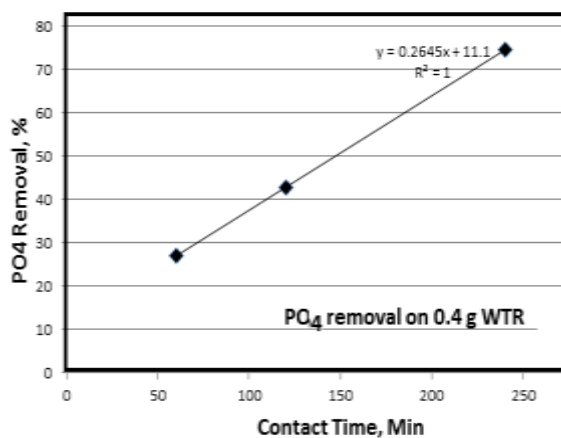


Figure 6: Phosphate removal curves.

The WTR also proved potential denitrification of water [15]. Makris et al. [16] studied the ability of WTR to immobilize excess soil phosphorus (P).

Kinetically, the WTRs exhibited a slow phase after a rapid initial phase. Maximum sorption capacity of Phosphorus sorption maxima 9100 mg of P kg⁻¹ was reported Methylene blue, MB, the dye is known in the application for the determination of soil properties including the cation exchange capacity, CEC, and specific surface area [17]. The methylene blue procedures yield an exact evaluation of some soil index properties. Further, they only need simple test equipment and are easy to apply.

4. Conclusion

The calcium-based water treatment residue proved a remarkable sorption activity towards dyes as a result of the relatively high surface area. The cation exchange capacity was comparable indicated a potential sorbent. The phosphate load of water can well be reduced using WTR and hence, a cheap soil amendment material to control the phosphate level may be recommended.

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