Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.922494

55 (2015) 970–977
July

Taylor & Francis
Taylor & Francis Group

Phosphorus removal from wastewater using rice husk and subsequent utilization of the waste residue

Mohammed Nsaif Abbas

Environmental Engineering Department, College of Engineering, The University of Mustansiriyah, Baghdad, Iraq, Tel. +964 78019163384; email: mohammed.nsaif.abbass@gmail.com

Received 4 June 2013; Accepted 1 May 2014

ABSTRACT

The removal of phosphor ions from an aqueous solution by adsorption by a low cost material, namely rice husk (RH), was investigated using different design parameters. The design parameters studied were the initial concentration of phosphorus (C_o) (1–100 mg/l), the absorbance media bed height (h_b) (10–100 cm), the pH of the phosphorus feed inlet (pH) (1-8), the treatment time (t) (1–60 min), feed flow rate (F) (5–100 ml/min), and feed temperature (T_f) (20–55°C). The results show that the percent removal efficiency decreased with increasing initial concentration and flow rate while it increased with increasing pH, absorbance material bed height, and feed temperature. The highest removal efficiency of phosphor ions achieved was 95.16% under optimum operating conditions ($C_o = 1$ mg/l), ($h_b = 100$ cm), and (pH 8), treatment time ($t = 60$ min), feed flow rate ($F = 5$ ml/min), and ($T_f = 55$°C). A statistical model was derived to find a general equation to relate all the operating parameters. Utilization of the huge amount of RH loaded with phosphor ions remaining after treatment in a useful method was also tested. One of these methods was to use the left over RH as cheap compost and this was tested for a tomato crop. In this way the process can present different benefits which are: to remove phosphor ions from contaminated water, to make good use of agricultural waste RH, and at the same time prepare a cheap fertilizer from the left over RH. This method can process a greater amount of waste in an economic and eco-friendly method.

Keywords: Rice husk; Phosphorus; Aqueous solutions; Adsorption; Residue and wastewater

1. Introduction

Phosphorus must be removed from wastewater as it provides a nutrient or food source for algae. Dead algae can cause hazardous oxygen depletion problems in receiving streams and it can kill fish and other aquatic life. Also, algae can cause other problems such as taste and odor in drinking water supplies. The contamination with phosphorus ions in surface and ground water comes from municipal wastewater containing detergents and concentrated agricultural waste including soil fertilization, feedlots, dairies as well as pig and poultry farms. The nutrient (phosphorus) is one of the leading causes of water quality pollution in rivers, lakes, and estuaries resulting in eutrophication, increased fish mortality, and outbreaks of microbes. If another source of high-quality phosphate is not identified, at the present rate of consumption the phosphate supply will be largely depleted in less than 100 years. This will place a burden on agricultural production as lower grade phosphates will have to be used, thus significantly increasing production costs [1]. Phosphates recovered from wastewater plants might be a viable source of industrial raw material for the manufacture of phosphate fertilizers. Currently, such phosphorus is regarded more as a contaminant than a resource, although this perspective has started to change in recent years [2]. The most common approach for removing phosphate from wastewater is precipitation with metallic salts because phosphate produces a precipitate with calcium, magnesium, or iron ions [3]. However, in the case of a lower concentration of phosphate, the removal is difficult and a greater amount of sludge is produced. Studies of phosphorus immobilization by adsorption have attracted a great amount of research interest in recent years directed at saving phosphate resources and recycling the phosphate. Some researchers have focused on activated alumina, iron-based compounds, layered double hydroxides, hydrotalcite, yttrium carbonate, and polymeric ligand exchange while others have placed more attention on natural materials and their modifications, such as boehmite and goethite [4], and even solid wastes, such as fly ash and blast furnace slag alum sludge [5–7]. Most of the environmentally difficult issues are concerned with the pollution of water by toxic metals [8]. At present, non-valuable and locally available agricultural biomaterials are being used as low cost materials for the remediation of pollutants from wastewater. Examples are the lignocellulosic waste of barley husk [9], rice husk (RH) [10], *Citrus sinensis* (sweet orange) [11,12], *Citrus sinensis* (mosambi) [13], rice milling waste [14], and peanut husk [15,16]. The aim of this current investigation is to study the possibility of using RH, which is considered as an agricultural waste, to remove phosphorus from a simulated synthetic aqueous solution (SSAS) and to benefit from the resulting RH loaded with residue in an eco-friendly manner.

2. Experimental work

2.1. Materials

2.1.1. Rice husk (adsorbent media)

RH was collected from Al-Shanafia rice fields in Southern Iraq. The RH was washed three times with doubled distilled water. Excess distilled water was used to remove the soluble materials present in the RH brought in from the field, boiled to remove the color and other fine impurities that may be found in the RH, and then dried at 105˚C for 24 h. The adsorbent processed in this manner was used in its original piece size. The surface area of the RH was measured by the BET (Brunauer–Emmett–Teller) nitrogen adsorption technique. The characteristics of the RH are presented in Table 1. When the RH was heated in an oven, most of the water was removed from the RH while the second major mass loss of about 45–65% was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue.

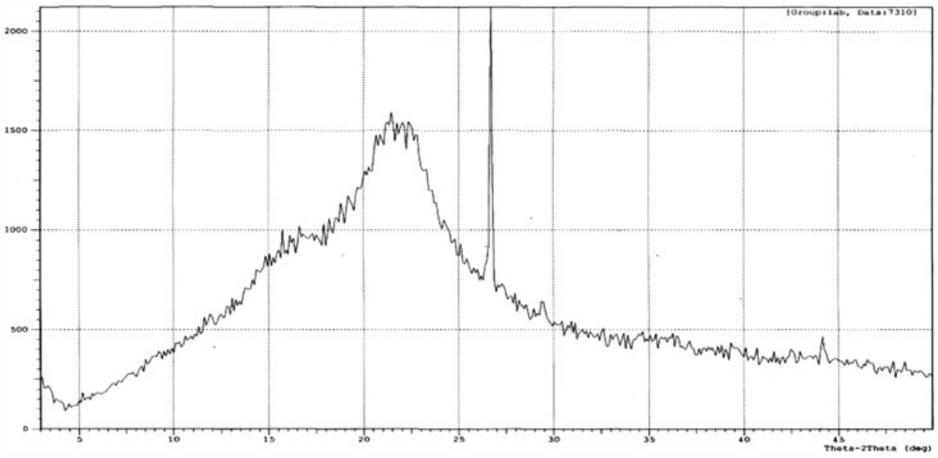
2.1.2. Stock solutions

In order to avoid interference from other elements in actual wastewater, the experiments in this study were carried out using a simulated synthetic aqueous solution (SSAS) of different phosphorus concentrations. A 1,000 mg/l stock solution of phosphorus was prepared by dissolving a known weight of (KH_2PO_4) in one liter of double distilled water. All solutions were prepared by diluting the stock solution with double distilled water to the desired concentration for the experimental work of this investigation. The phosphorus concentrations were measured using a spectrophotometer thermo-genesys 10 UV, USA.

2.2. Sorption unit

Continuous mode experiments were conducted using a fixed bed column in order to test phosphorus removal by separately treating individual SSAS solutions at the desired concentration of phosphorus at various bed heights of the adsorbent media RH using different flow rates of the SSAS phosphorous solution and at various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. A schematic representation of the sorption unit is shown in Fig. 1 where, the flow direction is downward by gravity. The sorption unit consisted of two glass containers of SSAS phosphorus solution, one container for the inlet and the other for the outlet, each of 1 liter capacity. The glass column had a 2.54 cm internal diameter (ID) and a height of 150 cm. The sorption column was packed with adsorbent media to a selected height (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 cm) and supported from the top and the bottom by a glass hollow cylinder layer, each cylinder being 0.5 cm ID, 0.1 cm thickness, and 1 cm long. Before starting the runs, the packed bed sorption column was rinsed by a flow of double distilled water down through the column. The RH was packed in the column to the desired depth, and fed as slurry by mixing the RH with distilled water in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was filled with the required amount of RH adsorbent media, the

Table 1
Characterization properties of Iraqi rice husk

Chemical composition		XRD of Iraqi rice husk
Compound	Composition wt%	
SiO_2	90.7	
Al_2O_3	0.13	
Fe_2O_3	0.06	
TiO_2	0.015	
CaO	0.61	
MgO	0.25	
Na_2O	0.09	
K_2O	2.64	
P_2O_5	0.73	
LOI	4.71	
S.A (m^2/g)	17.5	

adsorption process was started by allowing the SSAS phosphorus solution of the required concentration and pH to flow down through the sorption column from the inlet container by gravity at a precise flow rate in the experiment, which was adjusted by a valve as shown in Fig. 1. To determine the best operating conditions, the experiments were carried out at a range of temperatures (20–55°C), various pH values (1–8), and initial feed concentrations of SSAS of different phosphorus levels (1–100 mg/l). Each separate experiment used different flow rates (5–100 ml/min) for the phosphorus initial feed concentration. Outlet samples after treatment in each experiment were collected every 10 min from the bottom of a packed column and the un-adsorbed concentration of phosphorus in the SSAS was analyzed by a spectrophotometer.

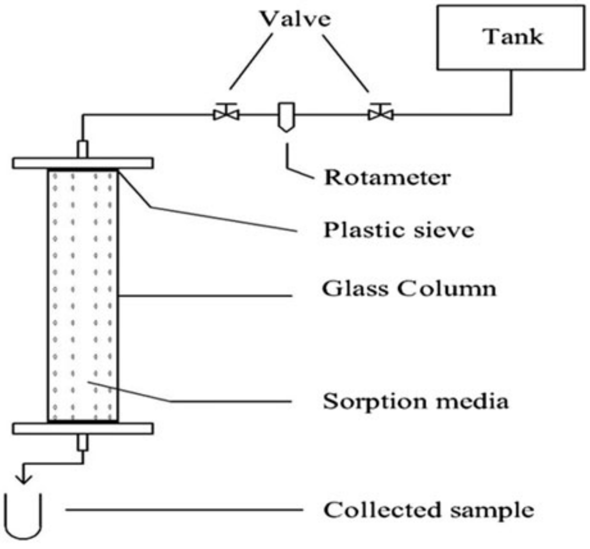


Fig. 1. The experimental adsorption unit.

2.3. Reusability of RH

In order to evaluate the reusability of RH as an adsorption media, RH loaded with different concentrations of phosphor ions was firstly dried and then used again in the sorption unit under the optimum operating conditions. The capacity of the adsorbent was found to decrease until it became constant. The removal efficiency and the number of times the same RH could be repeatedly used were found to depend on the phosphorus concentrations. Thus, *eleven times* repeated adsorbent use was seen to be feasible.

3. Results and discussion

The ability of RH to remove phosphorus from SSAS was investigated in a fixed bed column under continuous mode and various parameters which included the pH of the SSAS phosphorus solution (pH), the bed height of the adsorbent media RH (h), the flow rate of the SSAS (F), the SSAS temperature (T_{feed}), and the time of treatment (t). The experiments were achieved by varying all the above parameters for different initial concentrations (C_o) of the SSAS phosphorus solution. The results obtained are explained below.

3.1. Effect of initial concentration

The results indicated that using RH adsorbent material, the percentage removal of phosphorus decreased when the initial concentration (C_o) of the SSAS phosphorus solution was increased while the other parameters were kept constant as shown in Fig. 2. This can be explained by the fact that the initial concentration of phosphorus had a restricting effect on the capacity of phosphorus removal as simultaneously the adsorbent media had a limited number of active sites which became saturated at a certain concentration. This led to an increase in the number of phosphorus molecules competing for the available functional groups on the surface of the adsorbent material. Since a solution with a low concentration contains a small amount of phosphorus molecules compared to solutions with a high concentration, the percentage removal decreased with increasing initial concentration of phosphorus. For the adsorbent media, the highest percentage removal was 95.16% of phosphorus at an initial phosphorus concentration of 1 mg/l. Thus, the adsorbent material was found to be efficient for phosphorus removal from the SSAS and therefore from wastewater.

3.2. Effect of pH

The results showed that using RH adsorbent material, the percentage removal of phosphorus increased when the pH of the SSAS phosphorus solution increased, while the other parameters were kept constant as shown in Fig. 3. This increase can be attributed to the protonation of the RH surface which was caused by the species of phosphorus in the aqueous solution existing in the form of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, which forms a buffer solution in the aqueous solution. When the phosphate ions were adsorbed onto the RH, then H^+ was released from the solution and the concentration of H^+ resulted in a decrease of the pH of the solution [17]. In the situation when the pH increased, there was a competition between the hydroxide ions (OH^-) and phosphate ions in the aqueous solution, the former being the dominant species at higher pH values. The net positive surface potential of the sorbent media decreased, resulting in a reduction in the electrostatic attraction between the (*sorbent*) phosphate ions species and the (*sorbate*) adsorbent material surface (RH), with a consequent reduced sorption capacity which ultimately led to a decrease in the percentage adsorption of phosphate ions [18]. On the other hand, the adsorption of phosphorus ions could be explained by the ion-exchange mechanism of sorption in which the important role was played by the functional groups that had cation exchange properties. For this case, at lower pH values, the phosphate ion removal was inhibited, possibly as a result of the competition between the hydrogen and phosphorus ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricted the approach of the phosphorus ions as a consequence of the repulsive force. When the pH of the solution increased, the ligand functional groups in the adsorbent media (RH) would be exposed, increasing the negative charge density on the adsorbent material surface, thus increasing the attraction of the phosphate ions by the positive charge and allowing sorption onto adsorbent material surface.

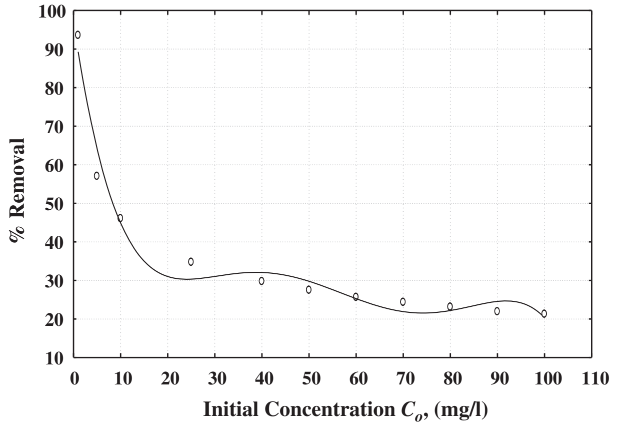


Fig. 2. Effect of initial concentration (C_o) on the percentage removal of phosphorus at $T_f = 55°C$, $h_b = 1$ m, pH = 8, $t = 60$ min, and $F = 5$ ml/min.

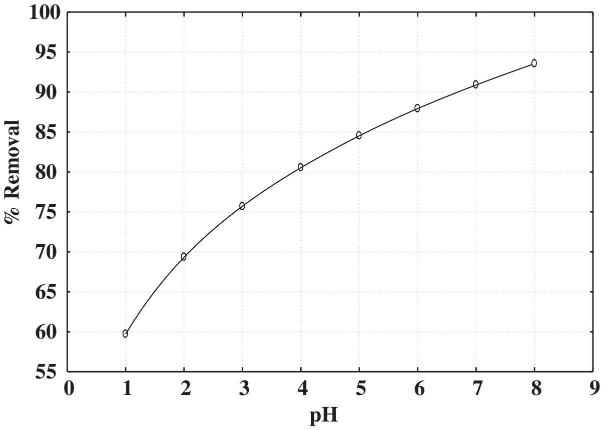


Fig. 3. Effect of pH on the percentage removal of phosphorus at $C_o = 1$ mg/l, $T_f = 55°C$, $h_b = 1$ m, $t = 60$ min, and $F = 5$ ml/min.

3.3. Effect of adsorbent media bed height

The results clarified that when the adsorbent media bed height was increased, the percentage removal of phosphorus was increased while the other parameters were kept constant as shown in Fig. 4. The increase in bed height (*h*) meant an increase in the amount of adsorbent media RH, thus increasing the surface area of the adsorbent material and hence increasing the number of active sites in the adsorbent material surface i.e. an increase of the availability of binding sites for adsorption and consequently an increase in the phosphorus removal capacity of the RH. This led to an increase in the ability of the adsorbent media to adsorb a greater amount of phosphorus from the SSAS for different initial concentrations and ultimately the percentage removal of phosphorus increased.

3.4. Effect of flow rate

The results illustrated that when the flow rate of the SSAS phosphorus solution was increased, the percentage removal of phosphorus was decreased while the other parameters were kept constant as shown in Fig. 5. When the flow rate increased, the velocity of the SSAS solution in the adsorbent media bed also increased, thus the solution spent a shorter time in the sorption unit; while at low flow rate the SSAS resides in the column for a longer time, and therefore undergoes more treatment by the adsorbent media. Thus, the adsorbent media would uptake only a low amount of phosphorus from the SSAS phosphorus solution for a high flow rate and therefore, the percentage removal of phosphor ions decreased when the flow rate increased.

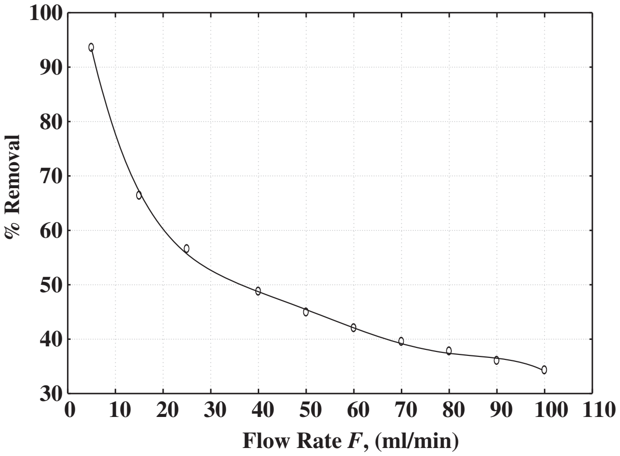


Fig. 5. Effect of aqueous solution flow rate (F) on the percentage removal of phosphorus at $C_o = 1$ mg/l, pH = 8, $T_f = 55$°C, $h_b = 1$ m, and $t = 60$ min.

3.5. Effect of feed temperature

The results demonstrated that when the temperature of the SSAS phosphorus solution feed was increased, the percentage removal of phosphorus also increased while the other parameters were kept constant as shown in Fig. 6. The effect of temperature was as expected and increased the mobility of the acidic ions. Furthermore, increasing temperatures may possibly have produced a swelling effect within the internal structure of the adsorbent media thus enabling the phosphorus ions to penetrate further. It

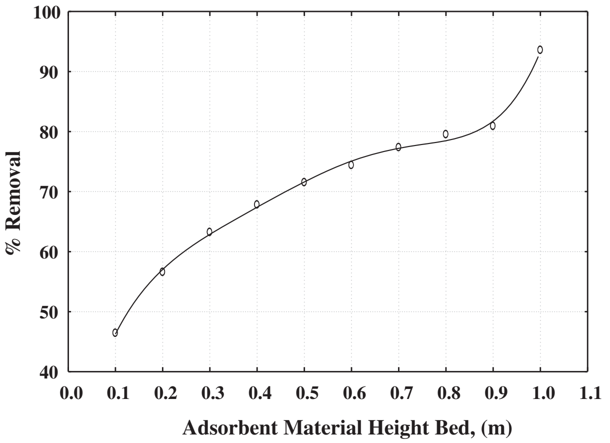


Fig. 4. Effect of adsorbent media bed height (h_b) on the percentage removal phosphorus at $C_o = 1$ mg/l, pH = 8, $T_f = 55$°C, $t = 60$ min, and $F = 5$ ml/min.

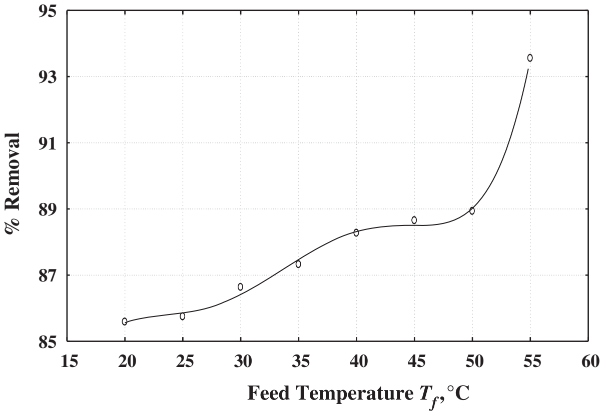


Fig. 6. Effect of feed temperature (T_f) on the percentage removal of phosphorus at $C_o = 1$ mg/l, pH = 8, $h_b = 1$ m, $t = 60$ min, and $F = 5$ ml/min.

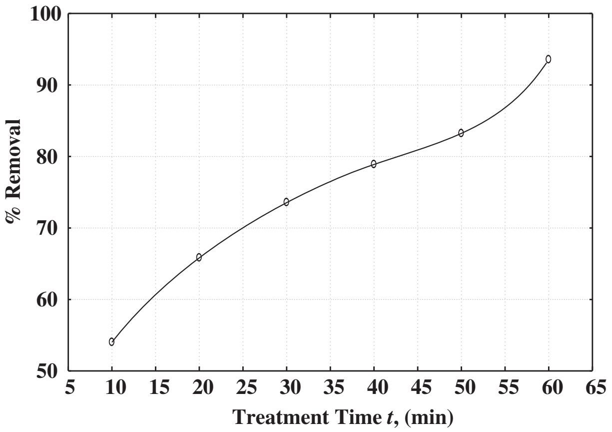


Fig. 7. Effect of treatment time (t) on the percentage removal of phosphorus at $C_o = 1$ mg/l, $T_f = 55$°C, pH = 8, $h_b = 1$ m, and $F = 5$ ml/min.

was indicated that the phosphorus adsorption capacity increased with increasing feed temperature from 5 to 55°C. This effect may be due to the fact that at higher temperatures an increase in active sites occurs due to bond rupture.

3.6. Effect of treatment time

The results established that when the treatment time of the SSAS phosphorus solution was increased the percentage removal of the phosphorus also increased, while the other parameters were kept constant as shown in Fig. 7. This may be due to the fact that when the time of treatment of the SSAS phosphorus solution increased and the velocity of the SSAS in the column packed with the adsorbent material remained constant, the solution spent a longer time in the sorption unit than when the time of treatment decreased, so the adsorbent material could uptake a greater amount of phosphorus from the SSAS. Therefore, the percentage removal of phosphorus from the SSAS increased with increasing treatment time.

4. Statistical model

A statistical model was determined for the experimental results obtained from this study. Regression analysis and the π theorem were adopted to maintain a relation between the percentage removal of phosphorus and the feed temperature, flow rate, pressure, pH of the feed solution, initial concentration of phosphorus, adsorbent media RH bed height, treatment time, and column diameter. These relations are shown in Eq. (1) below, which has a correlation coefficient (R^2) of 0.99.

$$\%R = 2.6634 \times 10^{-7}\left(\frac{T_f \times P \times h_b \times C_{\mathrm{P_{sol}}} \times t}{F \times d \times c_{\mathrm{o}} \times g}\right)^{0.297} (\mathrm{pH})^{0.216} \qquad (1)$$

where % R is percent removal of phosphorus from the SSAS, T_f is feed temperature, (K), P is pressure, (Pa), h_b is adsorbent material bed height, (m), C_{Psol} is heat capacity of aqueous solution, (J/g K), F is aqueous solution flow rate, (m^3/s), d is internal diameter of sorption column, (m), C_{o} *is* initial concentration of phosphorus, (g/m^3), t is treatment time, (s), g is acceleration due to gravity, (m/s^2).

5. Utilization of Iraqi RH after use

A huge amount of RH remained after using it for the removal of phosphorus from the SSAS as explained above. The RH can be utilized again as follows:

5.1. Employment of used RH as a fertilizer for tomato crops

Utilization of used RH can be achieved by applying it as a fertilizer for tomato crops as follows: RH waste which had previously adsorbed phosphorus from SSAS under different operating conditions was segregated and classified according to its phosphorus content and utilized as a raw material in the synthesis of a fertilizer for tomato crops. The samples had different ratios of phosphorus to RH. The ratios were between 0.01 and 0.1 wt% of phosphorus. The RH containing different ratios of phosphorus was firstly crushed to make a powder, the powder completely dissolved in water and then the tomato crop was irrigated using this solution. The tomato crop results showed good blooms and gave a higher weight crop (20.5 wt%) than the tomato crop irrigated with fresh water.

It is known that phosphorus increases the yield of crops, vegetables, and fruits, produces superior turf, as well as healthy and deep roots. It enhances the uptake of fertilizers, creates vegetation in saline and poor soils, and promotes ecological balance. Phosphorus can perform these actions as it enhances the soil structure and fertility through the addition of vital organic matter in the soil: by efficient transfer of fertilizer nutrients and micronutrients because of the high chelation and cation exchange proportion of the active phosphorus component, by increasing the moisture holding capacity of the soil, by increasing the microbial activity in the soil, and by enhancing plant cell biomass. Phosphorus has different effects on plant growth. It can have an effect physically through increasing the water holding capacity, increasing the aeration of soils, improving soil workability, helps resist drought, improves the seed bed, makes soil more friable or crumbly, and reduces soil erosion. Furthermore, it can have an effect chemically by chelating nutrients for uptake by plants, possessing a high ion-exchange capacity, increasing the buffering properties of soils, and increasing the percentage of total nitrogen in soils. Phosphorus can also have an effect biologically through accelerating plant cell division and promoting growth, increasing the germination of seeds and their viability, and increasing root respiration and formation. Stimulating growth and the proliferation of soil micro-organisms, aids in photosynthesis.

5.2. Employment of used RH in electric generation as a low value material

In many agricultural countries that are also producers of rice, such as Thailand, Malaysia, Sri Lanka, and others [19,20], the residual RH is used in the generation of electrical energy. Thus, it is possible to use RH to remove phosphorus from wastewater before using it again in the production of electrical power. In this way, two benefits are achieved from the use of RH whilst at the same time contributing to reducing the use of fossil fuels and thus preserving the environment in a more convenient and economical way by getting rid of two pollutants by one material.

6. Conclusions

The following conclusions can be drawn:

(1) RH showed a good ability to remove phosphorus from SSAS using a fixed bed adsorption unit. Hence, RH can be recommended for removal of phosphorus from wastewater in Iraq instead of other materials as it is valid, cheaper, economical, easy, and simple to use. Due to its high ability to adsorb phosphorus, can be used several times by easy regeneration and afterwards can be finally employed for another beneficial use.

(2) The maximum removal of phosphorus was 95.16% of the initial phosphorus concentration of 1 mg/l.

(3) The percentage removal of phosphorus increased with a decreasing flow rate of SSAS, pH, and initial concentration of phosphorus, while the percentage removal increased with increasing treatment time and the height of the adsorbent material RH.

(4) Used RH from water treatment can be prepared as a good fertilizer for tomato crops from the residual samples of RH that has previously adsorbed phosphorus from SSAS. Thus, the RH can remove the polluted waste in an economic and eco-friendly manner and also aid the tomato industry.

(5) The RH can also be used for generating electric power after using it to remove phosphorus from wastewater. Thus, two pollutants can be removed by one material in an economic and eco-friendly manner.

References

[1] Y. Tang, Z. Tong, G. Wei, Z. Li, D. Liang, Removal of phosphate from aqueous solution with modified Bentonite, Chin. J. Process. Eng. 6 (2006) 197–200.

[2] L.E. de-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), Water Res. 38 (2004) 4222–4246.

[3] L.J. Puckett, Identifying the major sources of nutrient water pollution, Environ. Sci. Technol. 29(9) (1995) 408A–414A.

[4] L. Li, R. Stanforth, Distinguishing adsorption and surface precipitation of phosphate on goethite (α-FeOOH), J. Colloid Interface Sci. 230 (2000) 12–21.

[5] K.C. Cheung, T.H. Venkitachalam, Improving phosphate removal of sand infiltration system using alkaline fly ash, Chemosphere 41 (2000) 243–249.

[6] L. Johansson, J.P. Gustafsson, Phosphate removal using blast furnace slags and opoka-mechanisms, Water Res. 34 (2000) 259–265.

[7] S. Huang, B. Chiswell, Phosphate removal from wastewater using spent alum sludge, Water sci. Technol. 42 (3–4) (2000) 295–300.

[8] M. Sindhu, K.M.M.S. Begum, S. Sugashini, A comparative study of surface modification in carbonized rice husk by acid treatment, Desalin. Water Treat. 45 (2012) 170–176.

[9] I. Haq, H.N. Bhatti, M. Asgher, Removal of solar red BA textile dye from aqueous solution by low cost barley husk: Equilibrium, kinetic and thermodynamic study, Can. J. Chem. Eng. 89(3) (2011) 593–600.

[10] Y. Safa, H.N. Bhatti, Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk, Desalination 272(1–3) (2011) 313–322.

[11] M. Asgher, H.N. Bhatti, Removal of reactive blue 19 and reactive blue 49 textile dyes by citrus waste biomass from aqueous solution: Equilibrium and kinetic study, Can. J. Chem. Eng. 90(2) (2012) 412–419.

[12] M. Asgher, H.N. Bhatti, Evaluation of thermodynamics and effect of chemical treatments on sorption potential of Citrus waste biomass for removal of anionic dyes from aqueous solutions, Ecol. Eng. 38 (2012) 79–85.

[13] H.N. Bhatti, N. Akhtar, N. Saleem, Adsorptive removal of Methylene Blue by low-cost Citrus sinensis Bagasse: Equilibrium, kinetic and thermodynamic characterization, Arab. J. Sci. Eng. 37(1) (2012) 9–18.

[14] H.N. Bhatti, Y. Safa, Removal of anionic dyes by rice milling waste from synthetic effluents: Equilibrium and thermodynamic studies, Desalin. Water Treat. 48 (1–3) (2012) 267–277.

[15] S. Sadaf, H.N. Bhatti, Batch and fixed bed column studies for the removal of Indosol Yellow BG dye by peanut husk, J. Taiwan Inst. Chem. Eng. 45(2) (2014) 541–553.

[16] S. Sadaf, H.N. Bhatti, Evaluation of peanut husk as a novel, low cost biosorbent for the removal of Indosol Orange RSN dye from aqueous solutions: Batch and fixed bed studies, Clean Technol. Environ. Policy 16(3) (2013) 527–544.

[17] S. Wang, C. Cheng, Y. Tzou, R. Liaw, T. Chang, J. Chen, Phosphate removal from water using lithium intercalated gibbsite, J. Hazard. Mater. 147 (2007) 205–212.

[18] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust, Chem. Eng. J. 84 (2001) 95–105.

[19] J. Prasara, T. Grant, Comparative life cycle assessment of uses of rice husk for energy purposes, Int. J. Life Cycle Assess. 16(6) (2011) 493–502.

[20] A.S. Rodrigo, S. Perera, Electricity Generation Using Rice Husk in Sri Lanka: Potential and Viability, National Energy Symposium, BMICH-Colombo, 2011, pp. 104–108.