

## Recovery of Phosphorus and Potassium from Industrial Effluents: Preparation of Magnesium-Potassium-Phosphate (Struvite-K) Fertilizer using Sea Bittern or Bittern based Salts

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### Abstract

Aim of present study is to recover phosphorus (P) and potassium (K) from effluents of chemical industries containing potassium carbonate and poly phosphoric acid via the precipitation of slow release fertilizer Struvite-K i.e. magnesium potassium phosphate hexahydrate (MKP;  $Mg.KPO_4.6H_2O$ ) or magnesium potassium phosphate trihydrate (MKP;  $Mg.KPO_4.3H_2O$ ). Sea bittern (a residual by-product from seawater solar halide production), kainite;  $[MgSO_4.KCl.3(H_2O)]$  or schoenite;  $[K_2Mg(SO_4)_2.6(H_2O)]$  type double salts are utilized as source of magnesium (M) or potassium (K). For preparation of MKP, stoichiometric mol ratio of the  $Mg^{2+}$  to  $K^+$  to  $PO_4^{3-}$  for reaction mixture was maintained at different pH values (9.5 to 7.5). Formation of MKP was confirmed using FTIR and P-XRD. TGA was used to investigate thermal stability and FE-SEM was used to elucidate morphology of crystals. Cost benefit assessment of the MKP produced has been done in detail. The method for preparation of MKP is simple and economic. Process will allow management of bittern in solar salt works and prevention of environment hazards of M, K and P release from chemical industries in oceans with financial gains.

**Keywords:** Fertilizers, Magnesium-Potassium-Phosphate; Struvite-K; Sea Bittern, Industrial Waste

## INTRODUCTION

Magnesium potassium phosphate hexahydrate,  $MgKPO_4 \cdot 6H_2O$  (MKP, Struvite-K), a slow release fertilizer is isomorphous with magnesium ammonium phosphate (MAP, Struvite) (1-4). Struvite-k crystals are found in natural minerals as well as in animal urinary calculi (5-8). The chemicals required for precipitation of MKP should contain Mg, K or P contents in appreciable amounts. For K requirements, mainly potash ore is the raw material. Majority of potash reserves are located in Canada and overall resources are not uniform around the globe (9). Looking at enormous usages of K, such reserves are likely to be exhausted in near future (10). Similarly, majority of the phosphate used for production of fertilizers comes from phosphate rocks, and the available resources of P will be exhausted soon (11-14).

Recovery of K and P from industrial effluents rich in K or P and sea bittern rich in M and K through precipitation of MKP can be a viable option. Therefore, new sources of potash fertilizers derived from bitterns and industrial effluents can be particularly attractive, especially for those countries lacking in potash ore. Several organic industries release potassium in various forms. Recycling of K in such instances is highly desirable. However, there have been limited studies on potential methods of K recovery (15). Likewise, several organic industries such as pigment industries are considered as most polluting industries and discharge large amounts of effluents containing very high amounts of P containing compounds along with other impurities. High P concentrations in effluents from wastewater pose greater threats to aquatic environments than total phosphorus runoffs from agriculture fields from phosphate rock fertilizer application (16,17). Therefore, P from such effluents can be alternatively utilized for fertilizers preparation such as MKP as natural P resources are depleting. In a recent review P recovery through struvite (MAP or MKP) crystallization and challenges for future designs has been critically discussed (18). Phosphorous recycling products for fertilizer effect have also been extensively reviewed (19). The influential factors of struvite crystallization process have also been reviewed in detail (20,21). In another report, it has been suggested that combinations of streams from different industries should be considered for process performance improvement (22).

The precipitation of MAP or MKP from urine or seawater has been well studied for recovery of P and K (23-27). MAP has also been efficiently crystallized using industrial effluents and bittern (28-30). However, the recovery of M, K, P as MKP from industrial effluents utilizing sea bittern or double salts obtained from bittern has been rarely investigated (31,32). In this report, we have used industries wastes, which contains significant concentration of K or P along with sea bittern or kainite/schoenite type double salts as source of M and K to precipitate MKP with good yield. The effective preparation of MKP by altering pH of the system will help in removal of P or extraction of K largely from waste effluents. This will also mitigate environmental hazards occurring due to effluent discharge. Further, MKP when dissolves in water, dissociate with a solubility of 0.215 g/100 ml of water (33). Utilization of MKP as efficient fertilizers for different soils is well established. Such a fertilizer can furnish M, K and P over for a prolonged time because of low solubility.

## MATERIALS AND METHODS

Effluents of industries having potassium carbonate and poly phosphoric acid were collected from a specialty chemical industry located in Maharashtra India and from a pigment preparations industry situated in Gujarat, India respectively. Sea bittern (magnesium rich liquor left after recovery of common salt from seawater) was used from Salt Production Unit of CSIR-CSMCRI, Gujarat, India. Kainite type double salt was obtained by fraction crystallization of sea bittern at high density, whereas schoenite type double salt was obtained from decomposition of kainite.

Effluents, solid products and filtrates were analyzed using ion chromatograph (IC) Thermo fisher, USA, 1CS 5000. Samples were prepared using milli-pore grade water. Prior to analysis, samples were filtered using 0.45  $\mu\text{m}$  membrane filters (Millipore). Analysis was conducted according to Standard Methods (34). Bittern and salt samples were analysed using standard techniques i.e.  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  concentrations through volumetric,  $\text{SO}_4^{2-}$  using gravimetric or  $\text{Na}^+$  and  $\text{K}^+$  by using flame photometry (35).

Magnesium potassium phosphate (MKP; Struvite-K) synthesis was done using potassium carbonate containing effluent (as K source), polyphosphoric acid containing effluent (as P source) and sea bittern (source of M and K) in stoichiometric ration. pH adjustments were done using NaOH. All the experiments were conducted in closed beakers. Solutions were stirred for 3-4 h for reaction completion, and kept for another 2-3 h to ensure complete precipitation. Filtrate free from potassium and phosphate ions and containing  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  was mixed to seawater required in solar salt works for production of common salt. MKP was characterized using PerkinElmer GX FTIR spectrometer and Philips X'pert MPD system. 10 scans with a resolution of 4  $\text{cm}^{-1}$  were made during FTIR measurements. FE-SEM (JFM 7100 F; Oxford Inc.) was used to study the morphology of precipitated crystals adopting the procedure reported in earlier paper (30). TGA/SDTA851 Mettler Toledo machine was used to for TGA. Heating rate of 10 $^\circ\text{C min}^{-1}$  was maintained during the measurements.

## RESULTS AND DISCUSSIONS

Prior to mixing the effluents containing K and P were characterized using analytical techniques. Analysis of K containing effluent is provided in Table 1 whereas P containing effluent is given in Table 2.

**Table 1:** Ionic composition of effluent containing K.

$\text{K}^+$ % w/v	$\text{Na}^+$ % w/v	$\text{CO}_3^{2-}$ % w/v
15.72	4.21	15.84

**Table 2:** Ionic composition of effluent containing P

PO <sub>4</sub> <sup>2-</sup> % w/v	Mg <sup>2+</sup> % w/v	K <sup>+</sup> % w/v	Ca <sup>2+</sup> % w/v	Na <sup>+</sup> % w/v	Cl <sup>-</sup> % w/v	SO <sub>4</sub> <sup>2-</sup> % w/v
20.5	0.04	0.01	0.09	0.15	0.09	0.02

Results indicate a concentration 15.75 % w/v of K and 20.5 % w/v of P content respectively in analysed effluents. Therefore, P and K salts can be effectively crystallized using the precipitation technique. Other ions such as Na<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, which are normally present in seawater are also present significantly in the effluents. Sea bittern, kainite and schoenite used for precipitation of K and P from effluents. The kainite type mixed salt used in this work was prepared from sea bittern through solar evaporation. Kainite mixed salt prepared from oceanic bittern was converted in one step into almost NaCl-free schoenite through a simple reaction-cum-leaching process as described in literature (36).



A portion of the mixed salt was treated under mechanical stirring for 3 h at room temperature (30-35°C) for this purpose. The high purity schoenite was then filtered. The analysis of sea bittern, kainite and schoenite type salts is provided in Table 3.

**Table 3:** Ionic composition of sea bittern, kainite and schoenite

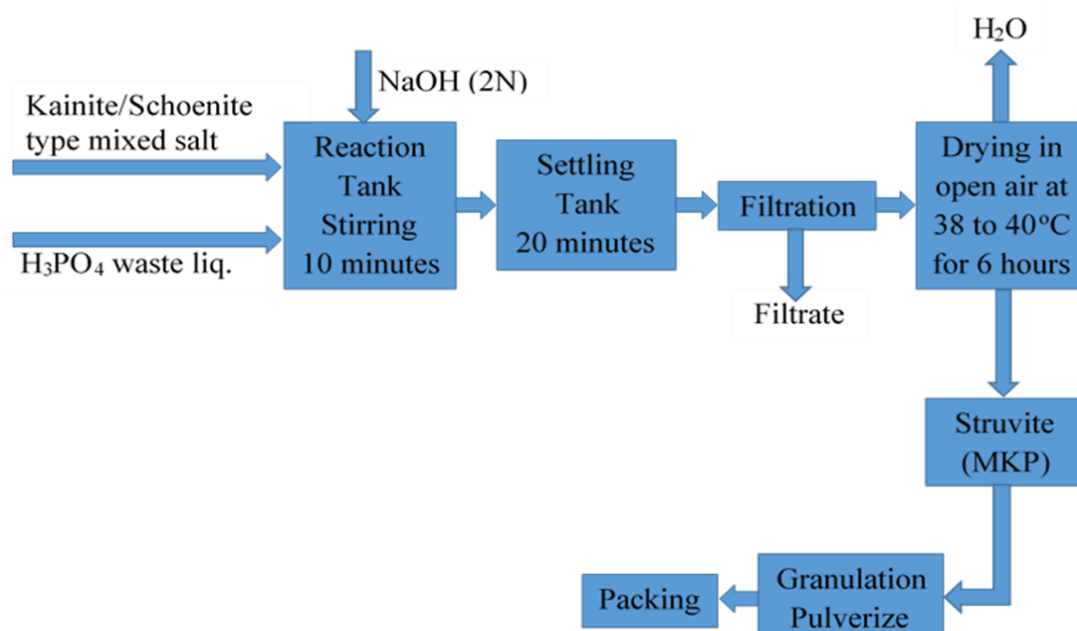
Samples	Specific gravity g/cm <sup>3</sup>	Mg <sup>2+</sup> (% w/v)	Ca <sup>2+</sup> (% w/v)	K <sup>+</sup> (% w/v)	Cl <sup>-</sup> (% w/v)	SO <sub>4</sub> <sup>2-</sup> (% w/v)
Bittern	1.2835	7.87	-	1.80	25.00	4.19
Kainite	-	5.81	0.03	5.06	30.32	27.21
Schoenite	-	6.52	0.12	16.99	3.68	50.04

Bittern, kainite and schoenite samples contained ~ 8, 6 and 6.5 % w/v of M content and ~ 2, 5 and 17 wt% w/v of K content. The quantity of ions is sufficient to extract P and K from waste streams in the form of MKP efficiently. It is reported that under alkaline conditions P, K and M containing solutions forms different hydrates of MKP; the most is MgKPO<sub>4</sub>·6H<sub>2</sub>O (37).



The reported optimal value of K:P ratio for MKP formation is more than 5 (24). Here, sea bittern, potassium carbonate waste/kainite or schoenite and poly phosphoric acid waste were mixed in stoichiometric ratio of Mg<sup>2+</sup> to K<sup>+</sup> to PO<sub>4</sub><sup>3-</sup> (1:1:1) mole ratio under variable pH conditions (9.0 to 7.5) using NaOH in order to crystallize MKP. pH of the resultant mixtures were optimized for effective precipitation. Depending on different

conditions viz. neutralizing time, digestion time, stirrer speed, temperature and bittern dilution pH value of 10 has been found highly suitable for the maximum recovery of M, K, and P (32). Here, for kainite type of salt effective precipitation was at 9.0 pH whereas for schoenite or potassium carbonate effluent as source of K, the precipitation was more effective at even lower pH (8.5). Solid crystalline white material was filtered and dried for further characterization. Complete scheme is shown below (Fig 1). The yield of MKP was found more at higher pH (9.0) when kainite type mixed salt was used. Under similar conditions of used raw materials, (50 g kainite in 200 ml water, 41 ml  $H_3PO_4$  containing effluent) yield of MKP decreased from 34.8 g to 28.5 g when pH was decreased from 9.0 to 7.5. The analysis of precipitated unwashed and washed samples (MKP-W and MKP-UW) prepared under different pH conditions and using different raw materials is provided in Table 4. Unwashed samples are contaminated with sodium and sulphate impurities which could be reduced by simple washing with water.



**Fig 1** Schematic description of MKP process.

**Table 4:** Ionic composition (% w/w) of precipitated MKP-W and MKP-UD samples using different sources and at different pH values

Source	Sample Details	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>2-</sup>	MgO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
Sea bittern	MKP-1W (pH-8.5)	8.3	2.8	5.4	1.6	31.4	13.8	6.5	23.5
Kainite type mixed salt	MKP-2UW (pH-9.0)	8.7	10.6	5.7	10.6	25.5	14.5	6.84	19.02
Kainite type mixed salt	MKP-2W (pH-9.0)	10.4	8.2	5.3	7.8	31.6	17.3	6.43	23.57

Source	Sample Details	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>2-</sup>	MgO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
Kainite type mixed salt	MKP-3UW (pH-8.5)	8.8	11.7	5.6	12.0	19.1	14.5	6.74	14.28
Kainite type mixed salt	MKP-3W (pH-8.5)	13.9	5.1	2.7	2.6	46.1	23.0	3.19	34.44
Kainite type mixed salt	MKP-4UW (pH-7.5)	9.04	1.17	5.4	14.0	21.3	15.0	6.48	15.91
Kainite type mixed salt	MKP-4W (pH-7.5)	15.54	4.44	1.6	3.71	43.5	25.8	1.92	32.51
Schoenite	MKP-5UW pH-8.5)	8.43	5.42	7.1	3.80	35.3	14.0	8.57	26.36
Schoenite	MKP-5W pH-8.5)	8.48	3.98	5.6	1.39	36.7	14.06	6.78	27.40

Simple washing with water or lean brines could reduce the impurities of sodium or sulphate ions. Table 5 shows the analysis of liquor left after recovery of MKP. Results indicate highly efficient removal of M, K and P from bittern and effluents. Minor contents of M or K left in filtrate can be extracted during the recycling experiments or by adjusting the molar ratio of constituents while precipitating MKP.

**Table 5:** Analysis of filtrate after MKP crystallization

Sr. No.	Sample Details	Mg <sup>2+</sup> % w/v	Na <sup>+</sup> % w/v	K <sup>+</sup> % w/v	Cl <sup>-</sup> % w/v	SO <sub>4</sub> <sup>2-</sup> % w/v	PO <sub>4</sub> <sup>2-</sup> % w/v
1	MKP-1	-	0.21	-	2.81	0.50	-
2	MKP-2	0.12	2.63	0.81	3.05	3.20	-
3	MKP-3	0.10	3.02	0.96	3.85	-	-
4	MKP-4	0.10	2.68	1.01	3.20	3.55	-
5	MKP-5	-	1.62	0.53	0.62	2.88	-

Quality of MKP crystals was ascertained using FTIR and P-XRD. Fig 2 shows the FTIR Spectra of MKP obtained under different conditions. FTIR spectra of MKP is reported in literature (1, 38). Therefore, the peaks are assigned accordingly. FT-IR spectroscopy can detect the H<sub>2</sub>O molecules of crystallization and their binding states in MKP. The spectrum of MKP reveals the existence of a broad, asymmetric, and complex feature between 3,800 and 2,500 cm<sup>-1</sup> (39). The broad, asymmetric band at 3500-2900 cm<sup>-1</sup> correspond to water symmetric stretching. Presence of water-phosphate H-bonding is indicated from the bands corresponding to 2300-2200 cm<sup>-1</sup>. The 1682 and 1600 cm<sup>-1</sup> bands are broad and asymmetric can be attributed to the existence of four crystallographically different types of H<sub>2</sub>O molecules in MKP crystal and indicate the H-O-H bending modes of vibrations (40, 41). The peak around 1000 cm<sup>-1</sup> represents PO<sub>4</sub><sup>3-</sup> asymmetric stretching (38). The peaks around 760 cm<sup>-1</sup> indicate water-water H-

bonding. The peaks around 570 and 450  $\text{cm}^{-1}$  correspond to P-O bend ( $\text{PO}_4^{3-}$ ) or Mg-O stretching vibrations (42). The band around 740  $\text{cm}^{-1}$ , can also confirm the presence of Mg-O bond (39).

**Fig 2** FTIR spectra of MKP precipitated in stoichiometric proportions of  $\text{Mg}^{2+}$  to  $\text{K}^+$  to  $\text{PO}_4^{3-}$  1:1:1. (MKP-1W) Using bitten and  $\text{K}_2\text{CO}_3$ ; (MKP-2W) using kainite type salt at pH=9.0; (MKP-5W) using schoenite type salt.

The crystalline phases and d-values obtained from the XRD have been compared with the JCPDS data. The XRD pattern of crystallized MKP samples (Fig 3) matched the database JCPDS (PDF-35-0812). The results indicated high phase purity and crystallinity of the precipitated material.



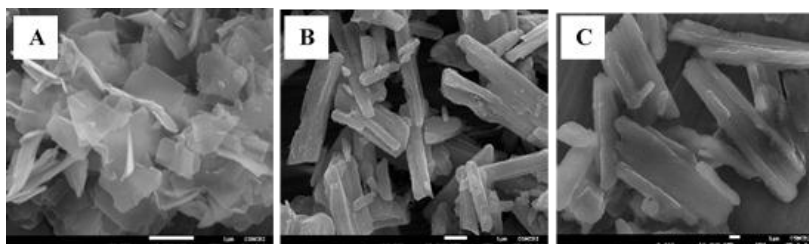
**Fig 3** P-XRD spectra of MKP precipitated in stoichiometric proportions of  $Mg^{2+}$  to  $K^+$  to  $PO_4^{3-}$  1:1:1. (MKP-1W) Using bittern and  $K_2CO_3$ ; (MKP-2W) using kainite type salt at pH=9.0; (MKP-5W) using schoenite type salt.

**Fig 4** TGA profiles of MKP precipitated in stoichiometric proportions of  $Mg^{2+}$  to  $K^+$  to  $PO_4^{3-}$  1:1:1. (MKP-1W) Using bittern and  $K_2CO_3$ ; (MKP-2W) using kainite type salt at pH=9.0; (MKP-5W) using schoenite type salt.

Thermal behaviour (0-750°C) of MKP samples was characterized from TGA profiles (Fig 4), which indicated that the process of decomposition initiated around 70°C and completed around 500°C. The initial major mass loss of the MKP begins at 70 °C and ends at 200 °C. The thermal profiles also indicated that the weight loss occurred in different manner for MKP precipitated using different sources. The major weight loss of about 42-44% occurred for MKP prepared using sea bittern and  $K_2CO_3$  containing effluent (MKP-1) or using schoenite (MKP-5), whereas approx. 20% weight loss occurred when MKP is prepared using kainite type of salts (MKP-5) indicating formation of hexahydrate and trihydrate crystals of struvite-K. The simultaneous loss of  $H_2O$  molecules from MKP crystals occurs gradually as a function of temperature rather than in distinct steps in case these are prepared using sea bittern or schoenite type salts as raw materials, whereas stepwise dehydration took place in MKP prepared kainite as raw material. Therefore, the dehydration of MKP in non-isothermal condition can be recognized as one-step dehydration as reported earlier (39).



SEM images (Fig 5) shows morphology of the MKP crystals grown from different raw materials. Images indicate that MKP crystals have been obtained in different morphologies viz. rectangular bar/sheets shapes. Both the ends of this micro crystals are flat. These morphologies may be due to the fact that, the microcrystals were not growing in lateral direction, but also in particular thickness (43).



**Fig 5** SEM images of MKP precipitated from different sources in stoichiometric proportions of  $Mg^{2+}$  to  $K^+$  to  $PO_4^{3-}$ . (A) MKP-1W; (B) MKP-1W; (C) (MKP-5W).

### Techno economic analysis of 1 TPD capacity plant

Techno economic feasibility of MKP production was evaluated using several parameters such as MKP production rates, chemicals consumptions, and engineering calculations. The economic viability of MKP production at pilot scale was derived using following indicators: (i) Plant establishment costs, (ii) capital expenditure (CAPEX), (iii) Operating expenditure (OPEX), and (iv) Cost recovery from MKP production (revenue). Basic engineering data of MKP preparation from kainite and schoenite routes for 1 ton/day capacity has been given in Table 6 and 7 respectively. From above data a payback period is found to be approximately 6.6 years. The data also indicate that production of MKP from different mixed salts and effluents will generate sufficient revenue, and the process is economically and technically feasible.

**Table 6** Basic engineering design of MKP production for using kainite type salt

Capacity of the Plant (TPA)	300
Basis	3 shifts/day, 300 Working days per annum
Design Basis	10% Design Margin
Capital Cost (Rs. in lakhs) (USD)	85.18 (\$1,19,252)
Production Cost (Rs. Per MT) (USD)	46937 (\$657)
Selling Cost (Rs. Per MT) (USD)	52500 (\$735)
Annual Sales revenue (Rs. in lakhs) (USD)	157.50 (\$2,20,500)
Annual Profit Before Tax (Rs. in lakhs) (USD)	16.69 (\$23,363)
Pay Back Period (Years)	6.23
Return on Capital Investment	10.62%
Break Even Point	71.94%

**Table 7** Basic engineering design of MKP production for using schoenite type salt

Capacity of the Plant (TPA)	300
Basis	3 shifts/day, 300 Working days per annum
Design Basis	10% Design Margin
Capital Cost (Rs. in lakhs) (USD)	85.18 (\$1,19,252)
Production Cost (Rs. Per MT) (USD)	47290 (\$662)
Selling Cost (Rs. Per MT) (USD)	52500 (\$735)
Annual Sales revenue (Rs. in lakhs) (USD)	157.50 (\$2,20,500)
Annual Profit Before Tax (Rs. in lakhs) (USD)	15.63 (\$21,883)
Pay Back Period (Years)	6.63
Return on Capital Investment	9.49%
Break Even Point	73.64%

**Assumptions:**

<i>Economic life of plant</i>	<i>10 Years</i>	
<i>Construction Period</i>	<i>6 months</i>	
<i>Capacity Utilisation</i>	<i>75%</i>	<i>1st Year</i>
	<i>85%</i>	<i>2nd Year</i>
	<i>100%</i>	<i>3rd Year onwards</i>

*No Interest as the capital cost will be met without loan.*

*No short term bank borrowings on working capital requirement.*

***Dollar Conversion Rate: 1 India Rupees = 0.014 US Dollar (as on 1st October 2020)***

The technology for N and P recovery has reached a high level of maturity and efficiency (44,45). There are several successful cases from wastewater treatment plants worldwide. In most of the methods of production of MKP it is necessary to provide an external source of Mg, such as MgCl<sub>2</sub>, MgO or Mg(OH)<sub>2</sub> which leads in higher cost (46). The pH range for effective struvite precipitation is between 7–11 and often sodium hydroxide is added to adjust the pH which also leads in increase of cost of the process (47). Here, bittern utilization, which is otherwise waste in solar salt fields not only fulfils the requirement of Mg but also reduces the usages of sodium hydroxide for raising the pH of the system. The liquor left after precipitation of MKP can be recycled into solar salt fields for recovery of common salt. Here the recovery of P and K from effluents is very high and overall the process is eco-friendly and highly efficient.

## CONCLUSIONS

Slow release fertilizer magnesium potassium phosphate (MKP) has been efficiently prepared by mixing industrial effluents containing P/K with sea bitterns or double salts extracted from sea bittern by adjusting mole ratio of chemicals and pH of the reaction mixture. MKP formation and its purity have been thoroughly characterized using an array of techniques. Process indicate very good recovery of P and K from effluents and possibility of reuse of bittern and P or K deficient waste in solar salt works. Techno-economic feasibility of the process is evaluated based on various engineering parameters and the process is found to be feasible and economic. The economic assessment of the production of MKP indicates potential profitability in the considered facilities. The expected revenues would exceed the operational expenses (OPEX), resulting in steady positive cash flows. The process will help utilization of industrial effluents and solar salt production discharge to get useful fertilizer thus creating waste to wealth along with mitigating health hazards.

## ACKNOWLEDGEMENTS

Communication number, CSIR-CSMCRI-81/2020. The analytical facilities of institute are acknowledged for sample characterizations. CSIR-CSMCRI in-house project MLP 0029 and MLP 0050 are also acknowledged.

## Conflict of interest.

The authors declare that they have no conflict of interest.

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